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Chemical etching of (1 0 0) GaAs in the $(NH_4)_2Cr_2O_7$–H_2SO_4–NH_4Cl–H_2O system

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The etching solution containing ammonium dichromate, sulphuric acid and ammonium chloride in water solution allows for the investigation of the influence of individual active components and their concentration on the etching reaction with GaAs. The influence of these agents on etching as well as the temperature and stirring were examined. The etching rate increases with increasing Cl^- ion concentration, increases and subsequently decreases with the increasing of H^+ ion concentration and remains constant in the wide range of oxidant anion concentration. The effect of stirring on etching rate allows us to estimate regions dominated by diffusion kinetics. The activation energy in the wide range of parameters is constant and equal to $60\,kJ\,mol^{-1}$. Microscopic observations reveal surfaces of various morphologies: smooth; covered with round hills; or with a network of veins. Various profiles of grooves arranged in various directions are revealed due to the preferential characteristic of etching; these profiles are also influenced by the mask material.

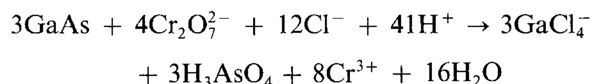
1. Introduction

Although chemical etching of semiconductor compounds $A^{III}B^{V}$ is still the subject of numerous investigations [1–8], few attempts have been made to examine in a more detailed way the chemical reaction occurring during etching, i.e. its kinetics and mechanism [9–11].

The present paper reports some results of investigations on (1 0 0) GaAs etching in the solution consisting of ammonium dichromate $(NH_4)_2Cr_2O_7$, ammonium cloride NH_4Cl and sulphuric acid H_2SO_4.

GaAs very easily undergoes etching reactions, thus the quantitative composition of etching solution may be varied in order to control the influence of individual components on the run of the etching reaction. The composition of the etching solution chosen for the investigation is in its general idea identical with that described by Adachi [12, 13], the only difference being that the sources of H^+ and Cl^- ions have been separated in order to study the effect of individual ion concentrations on the etching reaction run.

In the solution examined the etching reaction can be written in ion notation



$$3GaAs + 4Cr_2O_7^{2-} + 12Cl^- + 41H^+ \rightarrow 3GaCl_4^- + 3H_3AsO_4 + 8Cr^{3+} + 16H_2O$$

This reaction runs through a number of steps of which the most important are the following ones:

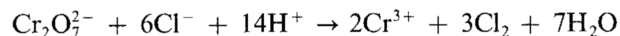
the oxidant ($Cr_2O_7^{2-}$) adsorption;

the oxidation: $GaAs - 8e \rightarrow Ga^{3+} + As^{(5+)}$;

the production of soluble products of oxidation (in reaction conditions these are: $GaCl_4^-$ ions and orto-arsenous acid or products of its partial dissociation).

The reaction is, moreover, accompanied with the phenomena of diffusion to or from the phase boundary which plays an important role in reaction kinetics, in spite of high concentrations of the solution components.

During examination of the GaAs reaction with the chosen solution account must be taken of another competitive reaction in which Cl^- ions are oxidized with $Cr_2O_7^{2-}$ ions



$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

This oxidation may be additionally catalysed by a semiconductor surface. The participation of this reaction in the etching process can be confirmed by the Cl_2 odour.

2. Materials and experimental procedure

The experiments were performed on (1 0 0) GaAs wafers chromium doped $\varrho = 10^7\,\Omega\,cm$ previously polished to a mirror-like surface. The etching solutions were prepared from adequate quantities of $(NH_4)_2Cr_2O_7$, NH_4Cl and H_2SO_4, analytical grade. In most cases the oxidant concentration was constant and equal to $0.5\,mol\,dm^{-3}$, H_2SO_4 concentration ranged from 0 to $6\,mol\,dm^{-3}$, i.e. assuming full dissociation H^+ changed from 0 to $12\,mol\,dm^{-3}$, Cl^- concentrations were 0.5; 1.5 and $2.5\,mol\,dm^{-3}$, being limited by NH_4Cl solubility. Higher concentrations of H^+, Cl^- and oxidant ions caused intensive evolution of Cl_2.

The GaAs surfaces taken for investigation were partially masked by wax or fotoresist AZ 1350, the height of steps were measured by a micrometre or profilogrammeter ME10. Most of the experiments were performed at room (296 K) and elevated (323 K) temperatures using thermostate. The etching procedures were performed in stirred and non-stirred solution. The mechanical stirrer was placed 25 mm

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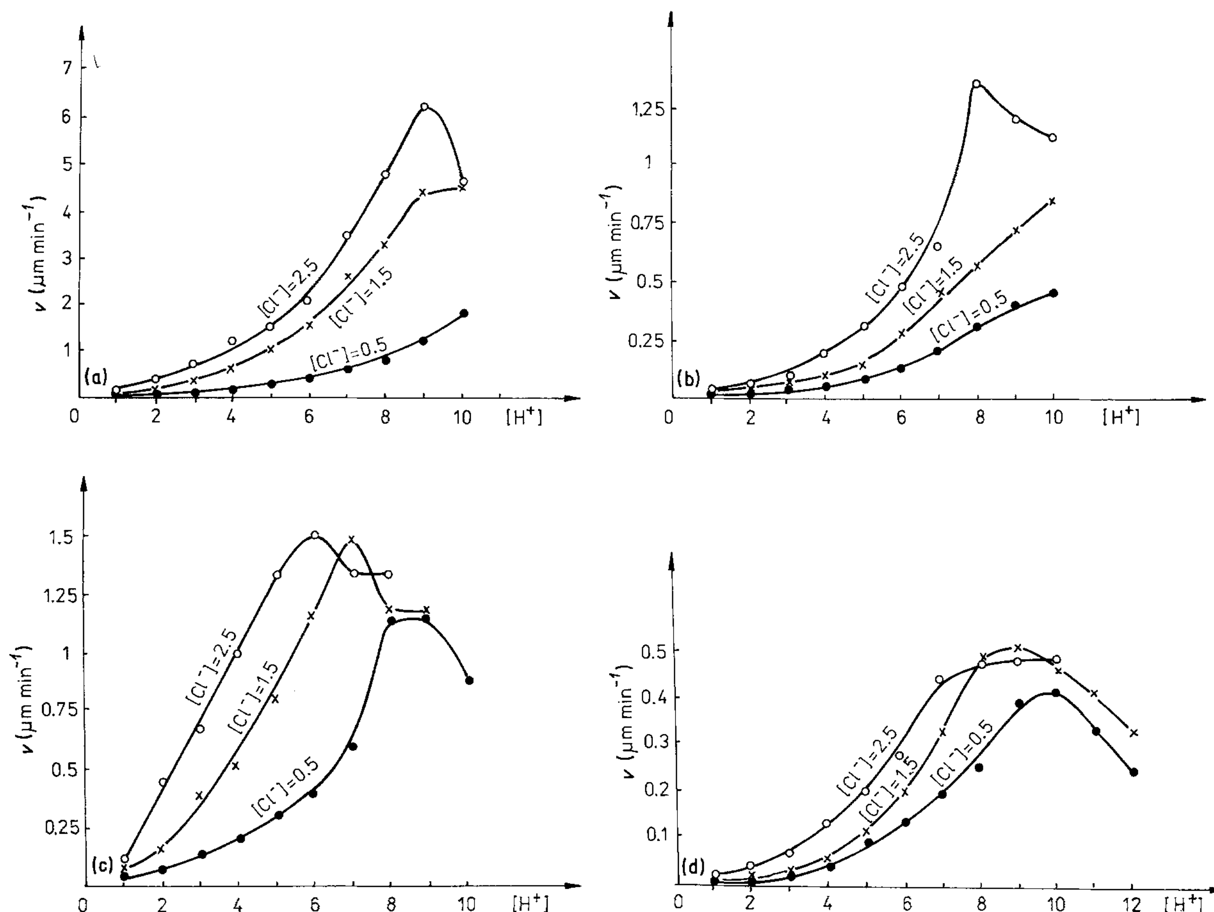

Figure 1 GaAs (100) etching rate against solution composition and etching conditions. In all the solutions used oxidant concentration was 0.5 mol dm^{-3}. (a) T = 323 K, stirred; (b) T = 296 K, stirred; (c) T = 323 K, non-stirred; (d) T = 296 K, non-stirred.

above the wafer. The changes in stirring intensity had no influence on the etching rate.

3. Effect of composition on etching rate

Etching rate against H^+ concentration for the selected Cl^- concentrations is shown in Figs 1a-d. The influence of oxidant concentration on the etching rate is shown in Fig. 2. It is worth noticing that the etching rate is constant in a wide range of concentrations of oxidant anions. Its decreasing over 0.6 mol dm^{-3} of $Cr_2O_7^{2-}$ concentration seems to be similar to that at high H_2SO_4 concentration. The results obtained in this run of experiments show that the etching rate ranging from 0 to 6 μm min^{-1} can be obtained when the reaction conditions are properly chosen. It should be noticed that the etching rate decreases when H^+ concentration exceeds a certain value. This decrease is especially distinct in high Cl^- concentration and when high etching rates are reached. This phenomenon seems to be due to the competitive reaction of Cl^- ion oxidization in which the indispensable reagents are being depleted.

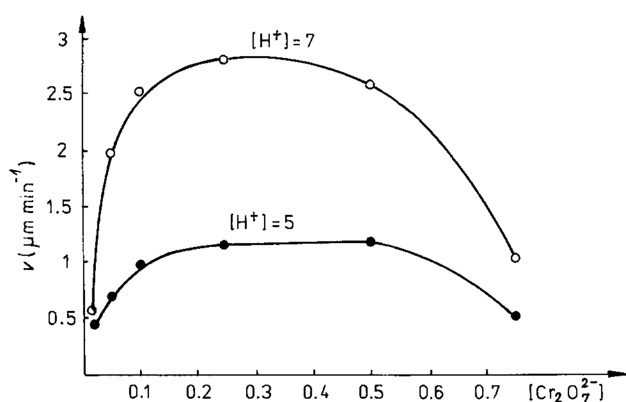

Figure 2 Etching rate against oxidant concentration $[Cl^-]$ = 1.5 mol dm^{-3} at 323 K with stirring.

To verify this hypothesis the Cl^- ions in solution were substituted by F^- ions (i.e. instead of NH_4Cl an equimolar quantity of NH_4F was introduced). It is obvious that F^- ions can by no means be oxidized with $Cr_2O_7^{2-}$ to free fluorine. Thus the competitive reaction cannot occur either. Moreover, because of the high complexing ability of F^- the occurrence of GaF_4^- or GaF_6^{3-} ions in place of $GaCl_4^-$ ions should be expected. Some examples of the results obtained are presented in Fig. 3. The results obtained for other etching conditions are of the same kind.

In the range of low H^+ ions concentration the rate of reaction with F^- is higher – probably due to the higher complexing ability of F^- compared with Cl^- ions. When H^+ concentration reaches 4 to 5 mol dm^{-3} both the rates became equal and then the etching rate with F^- is distinctly lower.

In the series of experiments conducted at 323 K the etching rate always reaches a maximum (as is shown in Fig. 3) and it drops with increasing H^+ ions concentration. In experiments carried out at room temperature the rates of reaction with Cl^- and F^- ions also became equal at an H^+ concentration of about

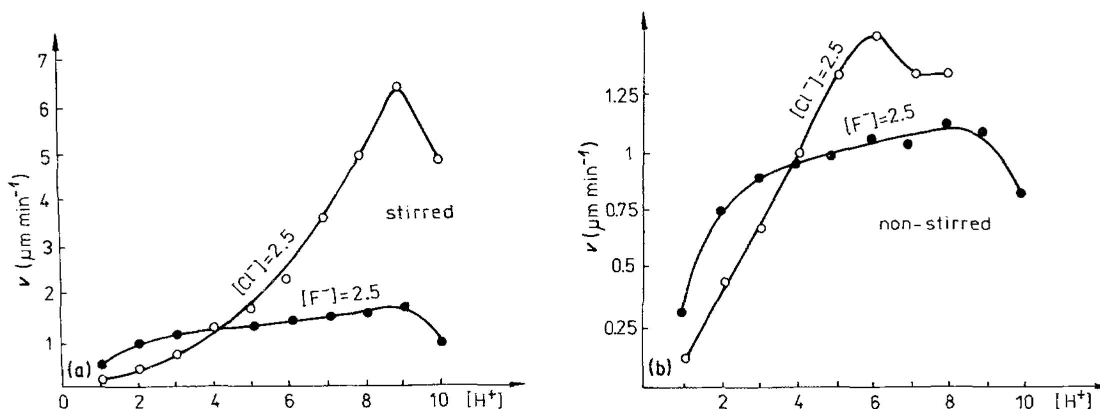

Figure 3 Effect of F^- ions on etching rate, $[Cr_2O_7^{2-}] = 0.5\,mol\,dm^{-3}$ at 323 K. (a) stirred; (b) non-stirred.

$5\,mol\,dm^{-3}$, but in the examined range it does not reach the maximum. In all the experiments without stirring the maximum rates of reaction with F^- reach about 80% of that with Cl^- ions. When the solutions were stirred the etching rate with F^- reaches scarcely 30% of that with Cl^- ions. The results of comparative investigations confirm neither the influence of a competition reaction on the etching rate nor a significant effect of the complexing abilities of F^-. Another suggestion is that the etching process especially in the range of medium H^+ ion concentration is influenced substantially by a "by-product" i.e. chlorine gas which is also a very strong oxidant.

Thus the problem of the drop of etching rate at high concentrations of H^+ ions has not been solved. Having stated that "chemical" reasons are not involved it seems that this fact may be due to other reasons:

(a) the competition of $Cr_2O_7^{2-}$ and SO_4^{2-} adsorption on the active centres on the GaAs surface;

(b) strong decrease of the activity of ions (especially H^+) at high concentrations; and

(c) more difficulty in the diffusion of substrate and products to/from phase boundary.

4. Stirring

The role of diffusion in kinetics may be estimated by examining the effect of stirring on etching rate. Assuming that the intensity of stirring in a wide range of speeds does not influence the etching rate, the results presented in Fig. 1 can be subjected to a comparative analysis. Results obtained for 323 K are presented in Fig. 4. The v_s/v_n ratio (v_s = rate with stirring, v_n = rate without stirring) is 1 (or close to 1) up to $v_s \sim 1.3\,\mu m\,min^{-1}$; when v_s exceeds this value, the rate is accelerated as the concentration of Cl^- ions is lower. From the facts presented above it may be inferred that up to $v_s = 1.3\,\mu m\,min^{-1}$ at 323 K the etching rate is determined by chemical reaction (kinetic range) whereas at $v_s > 1.3\,\mu m\,min^{-1}$, by diffusion to or from the phase boundary. Fig. 4 suggests that diffusion of Cl^- ions plays an essential role. At room temperature the stirring influence is manifested much earlier, i.e. at much lower reaction rates, and for Cl^- ion concentrations of $0.5\,mol\,dm^{-3}$ within the whole range being examined $v_s = v_n$.

From Fig. 1c it follows that the maximum rate at 323 K without stirring is $1.3\,\mu m\,min^{-1}$.

Comparing Figs 1 and 4 it may be seen that the decreasing rate with the increasing concentration of H^+ ions takes place mainly in non-stirred solutions. It may be expected that the drop in etching rate occurring in stirred solutions at higher concentrations of H^+ ions is also related to diffusion, this means that for such a high reaction rate (e.g. $v = 6\,\mu m\,min^{-1}$) the stirring velocity is too low.

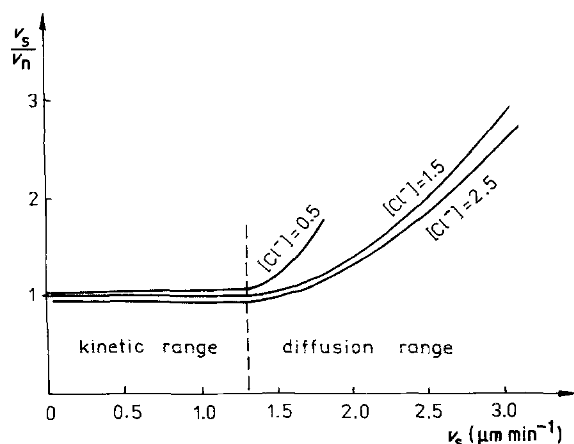

Figure 4 Effect of stirring on etching rate, v_s (etching rate with stirring) v_n (etching rate without stirring) $[Cr_2O_7^{2-}] = 0.5\,mol\,dm^{-3}$ at 323 K.

5. Temperature

More detailed information on the kinetics is provided by the measurements of etching rate as a function of temperature, from which the activation energy is determined. It is generally assumed that the processes, the activation energy of which is lower than $30\,kJ\,mol^{-1}$ ($6.5\,kcal\,mol^{-1}$) are controlled by diffusion and that higher values of activation energy give evidence that the process depends on the so-called kinetic factor, i.e. on the chemical reaction alone.

The activation energies of etching examined in detail for stirred solutions of different compositions are presented in Fig. 5. It may be seen that for a wide range of solution compositions, i.e. for a wide range of etching rates the activation energy is constant and equal to $60\,kJ\,mol^{-1}$. A slightly lower activation energy (about $50\,kJ\,mol^{-1}$) has been stated solely for solutions with low oxidant concentration. Constant values of activation energy suggest that in a wide range of concentrations the etching process is controlled by the same reaction stage and a high value of

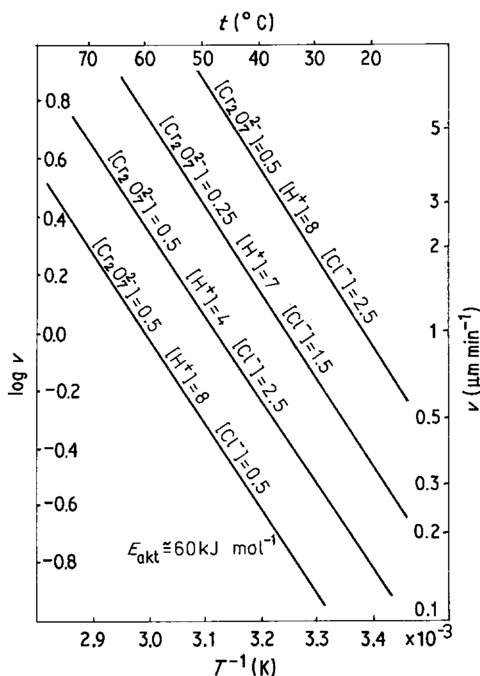

Figure 5 Activation energy of etching in stirred solution.

activation energy may be connected with a relatively low oxidizing ability of dichromate ions.

6. Etched surface quality

The quality of etched GaAs surfaces is of some importance as far as technological applications are concerned. The kinds of surfaces obtained in experiments carried out at 323 K without stirring can be classified into three groups corresponding to fields A, B and C in Fig. 6. In field A the surfaces are smooth, covered with a clear network of veins, the intensity of which decreases in the direction of field B. The surfaces obtained in field B are smooth and satisfactory for technological applications. The field B equals to a 1 to 1.5 μm min^{-1} etching rate. In field C the surface is also smooth and mirror-like, but is covered with round hills a few micrometres high and several tens of micrometres in diameter. Their origin is discussed by Weyher [14, 15]. It seems that in very active solutions (field B) the Cl_2 evolution is accompanied by simultaneous reaction in which free oxide is produced

$$Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3/2O_2 + 4H_2O$$

The evolved gas in form of bubbles may protect some round places against etching.

During etching without stirring at 296 K, the surface state is similar to fields A and C. The field B disappears, smooth surfaces are not obtained, the line dividing two fields (A and C) corresponds to a 0.4 to 0.5 μm min^{-1}. etching rate.

Etching with stirring gives always surfaces as for field A. Only strongly acidic solutions (H^+ 9 to 10 mol dm^{-3}) with high Cl^- ions concentration give smooth and mirror-like surfaces. It can be stated that good quality surfaces are obtained at etching rates at which the mechanism is changed (from kinetics to diffusion) regardless of whether the solution is stirred or not.

In the case of other semiconductor materials, such

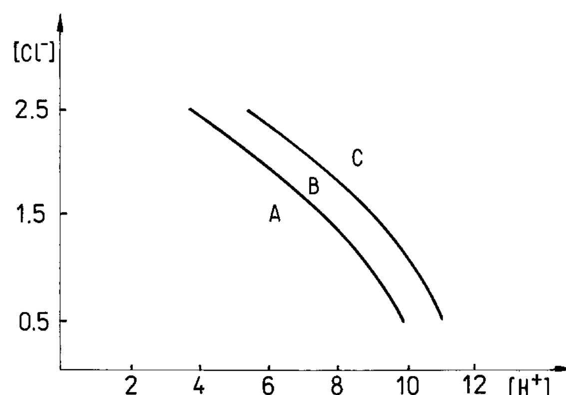

Figure 6 Effect of etching conditions on surface quality, $[Cr_2O_7^{2-}]$ = 0.5 mol dm^{-3} at 323 K, without stirring.

as silicon or germanium, diffusion controlled etching results in polished surfaces, whereas in etching controlled by a kinetic mechanism structural defects are revealed [16–19]. By analogy it may be supposed that in the kinetic range there appears an irregular network on the GaAs surface while surface polishing takes place in the diffusion range. The polishing is, however, disturbed by gases evolved in competing reactions. The intensity of gas evolution increases with increasing concentration of H^+ ions. Surfaces obtained by very slow etching rates (i.e. at low H^+ ions concentrations such as 2 to 3 mol dm^{-3}) do not follow the above principles.

Generally, the surface state depends on the solution composition and on other parameters of etching (stirring, temperature) and etching time.

The range of solution composition in which smooth surfaces are obtained is limited and the results (e.g. dependence on etching time) do not have good reproducibility. This range cannot be useful in technological processes in which a good smooth surface is required.

7. Etching profiles

Etching of GaAs (1 0 0) in acidic solutions is anisotropic. In order to understand this phenomenon better, a series of narrow grooves arranged [1 $\bar{1}$ 0], [1 0 0], [1 1 0] and [0 1 0] on the (1 0 0) planes were etched through SiO_2 or AZ 1350 resist masks.

The grooves were etched in solutions containing H^+ ions with concentration 7 mol dm^{-3}; Cl^-, from 0.5 to 2.5 mol dm^{-3} and $Cr_2O_7^{2-}$, from 0.02 to 0.75 mol dm^{-3}. The shapes of grooves etched through windows in the SiO_2 mask do not depend on etching solution composition and are always like those shown in Fig. 7a.

Selected examples of the shapes of grooves obtained in various stirred solutions (always at 323 K) in the presence of the AZ 1350 mask are shown in Fig. 7b. No tendency towards rounding of the groove bottom has been observed.

Etched grooves were wider than mask windows. The groove width increase defined as the ratio of the half-width increase to the groove depth, depends on the mask alignment and on the mask material.

The influence of etching bath composition on groove width increase is negligible. The width increase rate values obtained in various conditions are given in Table I.

$[Cr_2O_7^{2-}]$	$[Cl^-]$	$[H^+]$	$(1\bar{1}0)$	(100)	(110)	(010)
0.1 ⋮ 0.75	0.5 ⋮ 2.5	7	α	β	γ	δ
(a)			α = 45°	β ≅ 90°	γ = 103°–117°	δ ≅ 90°

$[Cr_2O_7^{2-}]$	$[Cl^-]$	$[H^+]$	$(1\bar{1}0)$	(100)	(110)	(010)
0.02	1.5	7	α			
⋮ 0.75			α	β	γ	δ
0.5	0.5	7	α	β	γ	δ
	⋮ 2.5		α	β	γ	δ
0.25	1.5	3	α	β		δ
		⋮ 7	α	β		δ
			α = 25°–30°	β = 60°–70°	γ = 90°–110°	δ = 60°–70°

(b)

Figure 7 Shapes of grooves etched on GaAs (100) of 20 μm, depth, etching temperature 323 K, with stirring, (a) in presence of SiO_2 mask and (b) in presence of AZ 1350 mask.

The AZ 1350 resist masks show very poor adherence to the wafer surface in comparison to the oxide masks, so their use leads to a larger increase in the groove width. Such grooves show various profiles and are not repeatable, this is especially visible for the [1 1 0] orientation where width increase is of the most significance.

It is worth mentioning that for the $[1\,\bar{1}\,0]$ as well as for the [1 1 0] orientations the groove shapes depend on the masking material (AZ 1350 or SiO_2). Expected planes $(111)_A$ giving angles of 54 or 126° are not revealed in any case. Planes reported by other authors [8, 11] revealed in the presence of resist masks were also of various types and none of them was "simple" (111). Even so the repeatable angles of 45° for the $[1\,\bar{1}\,0]$ directions obtained in the presence of the SiO_2 mask does not coincide with any low-index plane in the GaAs crystal lattice. It can be stated that the side walls of the grooves are not simply crystallographic planes but they are rather arrays of surface steps on the (111) plane [11].

The assumption that the groove profile is greatly determined by the adhesion of the mask material to the wafer surface is supported by the above considerations. Moreover, this same mask material can show different adhesion towards various etching baths, hence the grooves revealed in etching presented in this paper (and many others) are of various shapes.

One may conclude that it is doubtful if the AZ 1350 masks are the best ones for groove or MESA structures etching, apart from the good resistance of AZ 1350 against the etching solution.

8. Summary

The results presented above do not allow us to define unequivocally the mechanism of etching. There are some premises that this mechanism depends on the solution composition and etching conditions. (e.g. the drop of etching rate after a critical H^+ ion concentration is exceeded (Figs 1 and 2) is certainly related to the change of etching mechanism.)

The experiments carried out with the fluoride anions, especially in higher H^+ ions concentrations, suggest that chlorine is a by-product of GaAs oxidation.

The minimal effect of stirring intensity on the etching process indicates a significant role of the chemical reaction occurring on the phase boundary and the negligible one of diffusion. This assumption is confirmed by the high activation energy (60 kJ mol^{-1}). A high energy barrier is connected with a relatively low oxidating ability of $Cr_2O_7^{2-}$ ions. The activation energy of GaAs etching in acidic solutions of such a strong oxidant as hydrogen peroxide range between 25 and 45 kJ mol^{-1} [3, 9].

The drop in activation energy observed for low

TABLE I The groove width increase

mask material	Orientation			
	[1 1 0]	[0 1 0]	$[1\,\bar{1}\,0]$	[1 0 0]
AZ 1350	1.91 ± 0.39	1.44 ± 0.25	0.92 ± 0.36	1.44 ± 0.22
SiO_2	0.68 ± 0.08	1.03 ± 0.09	0.40 ± 0.05	1.04 ± 0.07

oxidant concentrations shows that this reaction is sensitive to this agent.

The anisotropy of the etching process, i.e. that some crystallographic planes are privileged is closely related to the mechanism of this reaction, its steps, sequence and rate, as well to the kind of mask material.

The practical aspects of the results obtained are the following ones:

(a) although the AZ 1350 photomask is resistant to the etching action of the reported etch bath, the oxide mask leads to better defined groove shapes and dimensions;

(b) the etching baths are relatively stable (especially those with low H^+ concentration) and provide a good reproducibility of kinetic data;

(c) profile shapes are reproducible, groove walls are smooth, the differentiation of shape in four basic directions is less distinct than in other solutions used for GaAs etching;

(d) the surface state depends substantially on the conditions and time of etching as well as on the composition of the solution, thus whenever the surface smoothness is an important parameter, such solutions cannot be used without any limitations.

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