Chemical etching of (1 0 0) GaAs in a sulphuric acid–hydrogen peroxide–water system

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A detailed investigation of the etching of (1 0 0) GaAs in H_2SO_4–H_2O_2–H_2O systems has been made. The influence of the concentration of particular etchant components on etching rate and on the shape of the crystal surface was examined. From these results the Gibbs' triangle of etching bath compositions was divided into parts corresponding to the various states of the crystal surfaces and various etching mechanisms. The shape of the crystal surface after etching was closely related to the profiles of the grooves etched in the [1 1 0] direction in the same solution.

1. Introduction

Investigation of the chemical etching of (1 0 0) GaAs in a solution consisting of sulphuric acid, hydrogen peroxide and water is of technological and scientific importance [1]. This solution is often used for the preparation of a surface in the sequence of operations in the course of the manufacture of semiconductor devices. For this reason the solution should be optimized; on the other hand, the results obtained constitute a good starting point for the discussion of heterogenous reaction mechanisms.

The sequential chemical reactions taking place on the phase boundary are: the diffusion of reagents from solution to phase boundary; the adsorption of reagents on the solid surface; the oxidation process; transformation of oxidation products to the ionic form; desorption; diffusion of products into the solution.

Reagents in the solutions considered are H_2O_2 molecules and H^+ ions similar to in the H_3PO_4–H_2O_2–H_2O system [2]. The flow of reagents to the solid surface depends on their concentration and on solution viscosity, i.e. indirectly on the H_2SO_4 concentration. The adsorption generally takes place on the so-called active centres of crystal surface depending on surface orientation. In some cases, etching reveals a crystal structure.

During oxidation, the adsorbed H_2O_2 molecules accept electrons from GaAs which in turn becomes Ga^{3+} and As^{3+} or As^{5+}. Oxidized atoms of gallium and arsenic penetrated to the solution as Ga^{3+} ions and orthoarsenic acid (H_3AsO_4) molecules, or its partial dissociation products, through sulphuric acid [2, 3].

Both desorption and diffusion depend on the concentration and the viscosity of the solution.

The final state of the etched surface is determined by the partial process with the highest energetic barrier (i.e. the slowest). If the slowest process is adsorption and, in consequence, oxidation, the process must be controlled by chemical reactions. If the etching rate is limited by diffusion, it is then called a "diffusion-controlled process". The activation energies higher than $6.5\,kcal\,mol^{-1}$ correspond to kinetic reaction (chemically limited) while the lower energies indicate a diffusion-type etching process. Etching controlled by product dissolution and its diffusion from the phase boundary may result in a polished surface. The influence of etching conditions on the semiconductor surface quality was investigated in detail by Schwartz [4].

2. Experimental procedure

The range of solution concentrations of the H_2O–H_2O_2–H_2SO_4 system used in the experiments was limited by the available concentrations of reagents. The composition of the solutions is commonly described by volume percentage on the Gibbs' triangle, its vertices being water, $30\,wt\,\%$ hydrogen peroxide and $96\,wt\,\%$ sulphuric acid. High concentrations of sulphuric acid in the solution result in partial hydrogen peroxide decomposition. To estimate the stability range of the solutions, they were titrated with $KMnO_4$ immediately after the components were mixed, and then after 2 and 24 h. If the results of the analyses differed by less than 5% from the calculated compositions and were stable as the same level, the solutions were considered to be stable. The stability line at room temperature corresponds to $50\,vol\,\%$ H_2SO_4 without stirring, and a little below this value in stirred solutions, as shown in Figs 1 and 2. All solutions were prepared by mixing proper quantities of H_2SO_4 with H_2O and cooling to room temperature. H_2O_2 was then added slowly to avoid temperature increase. For discussion of the reaction kinetics and mechanism it is convenient to present the solution composition as molar percentage. The range of usable compositions is shown in Figs 3 and 4.

The experiments were performed on chromium-doped semi-insulating (1 0 0) GaAs wafers ($\varrho = 10^5\,\Omega\,m$). The etching rates were controlled over the whole solution concentration range. H_2SO_4 and H_2O_2 concentrations varied by 5 or $10\,vol\,\%$. To estimate the etching rates, the heights of steps were measured
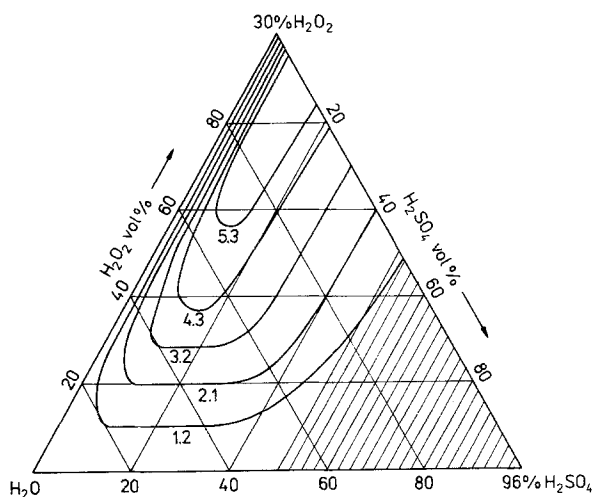
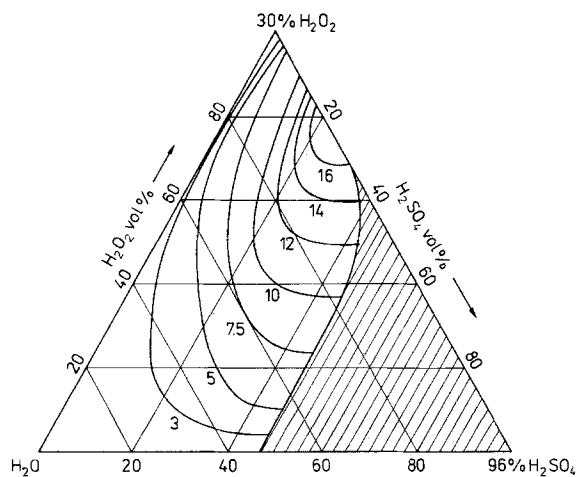*Figure 1* Constant etching rate contours for (1 0 0) GaAs (μm min^{-1}) for unstirred solutions.

Figure 2 Constant etching rate contours for (1 0 0) GaAs (μm min^{-1}) for stirred solutions.

(using a micrometre with accuracy of 1 μm) on a surface partially masked with wax or photoresist. The heights were of some tens of micrometres. All etchings were performed at 21 to 23° C; the higher temperature caused accelerated decomposition of H_2O_2 molecules, and thus limited the range of stable solutions. For this reason activation energies requiring a wide range of temperatures for estimation, were unattainable.

In the etching procedures which were stirred, the etched wafers were intensively swung manually. The changes in stirring intensity had no influence on the etching rate and resulting surface quality. The quality of etched surface was examined by scanning electron microscopy whereas the shapes of the grooves etched in the wafers were observed under an optical microscope.

3. Results and discussion

The results of etching are presented as lines linking the points of the same etching rates in the field of the Gibbs' triangle and as curves showing the etching rate dependence on one component concentration assuming the concentration of the other components to be constant. The results obtained during etching without stirring are presented in Figs 1. 3, 5, 6 and with stirring in Figs 2, 4, 7, 8. Moderately driven stirring enhances

the reagent diffusion to/from the phase boundary, thus increasing the dependence on the chemical reaction. Comparison of the results obtained with and without stirring leads to significant conclusions, presented in Figs 9 and 10, in the form of a Gibbs' triangle, in which the fields corresponding to similar surface states and with similar etching mechanisms are indicated.

Comparing the results of kinetics measurements with surface state observations given in the Figs 11 and 12, some interesting observation may be made. In the whole range of low H_2SO_4 concentration (field a in Fig. 9), i.e. up to ~ 4 mol % H_2SO_4, the pictures of surfaces obtained by etching are identical. The surface morphology in form of figures of some micrometres in size is clearly visible in Fig. 11a. From the shapes of the curves in Fig. 7, as well as from the anisotropic type of the etched surface, one may conclude that in this composition range the etching mechanism is the same and the controlling reaction is surface oxidation, concentrated in the so-called active points. Etching is selective. The lack of dependence of the surface state on oxidative concentration and the significant increase in etching rate with increase in H_2SO_4 concentration up to 4 mol % seem to exclude the selective oxidation of the surface. This inconsistency may be explained if
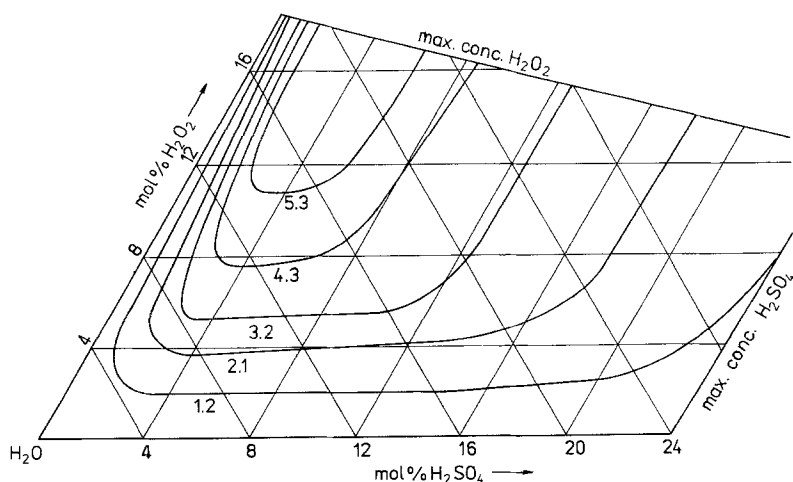

Figure 3 Constant etching rate contours for (1 0 0) GaAs (μm min^{-1}). Unstirred solutions. Etching bath composition in mol % %.
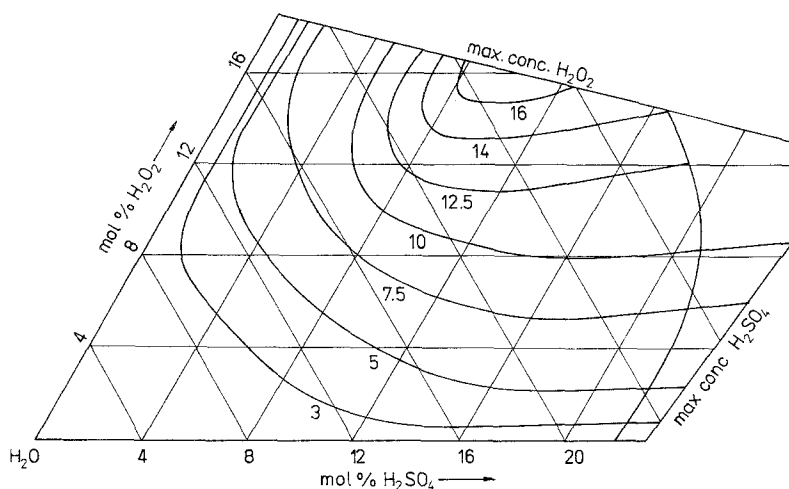
Figure 4 Constant etching rate contours for (1 0 0) GaAs (μm min^{-1}). Stirred solutions. Etching bath composition in mol % %.

one assumes that the oxidation ability of H_2O_2 molecules is connected only with their activation with H^+ ions. Thus the etching remains selective even at large concentrations of oxidant while etching proceeds and its results are influenced by a minority factor, i.e. acid, which is responsible for the transformation of reaction products to the ionic form and results in a smooth surface. It may be concluded that sulphuric acid actively takes part in the oxidation reaction, probably by the activation of H_2O_2 molecules. The oxidation rate may be fixed as

$$V_{ox} \sim [H_2O_2]^a [H_2SO_4]^b$$

In the same range of solution compositions, i.e. up to 4 mol % H_2SO_4 which were not stirred, the etching rate is the same as in the stirred solutions (Figs 5 and 6). This supports the hypothesis of the dominant role of a chemical factor in the etching procedure. The surfaces states (Figs 12a, b and 11a) are also similar, regardless of stirring.

With increase in the oxidant agent concentration, the figure sizes became larger, and at the highest avail-

able H_2O_2 concentration (~ 18 mol %) the surface is covered with a white deposit, which is amorphous, but loses approximately 25% of its weight and becomes crystalline when annealed in 300° C. Diffraction patterns of this product are very complex, with fundamental lattice plane distances of 0.391 and 0.351 nm. It is probably gallium arsenate. The deposit (Fig. 12c) is soluble in sulphuric acid. In the range of solution compositions in which the deposit occurs, the sulphuric acid concentration is too low to dissolve this product at a sufficient rate to enable the chemical reaction to be traced. An increase in sulphuric acid concentration over 4 mol % in the stirred solutions caused a further etching rate increase and then its stabilization. A slight decrease of etching rate occurs at the beginning of H_2O_2 decomposition, as mentioned above. Wafer surfaces are mirror-like (Fig. 11b) i.e. etching conditions fulfil the requirements for surface polishing, the diffusion of reagents being a limiting factor. A range of low oxidant concentrations is an exception (Fig. 9c): according to general rules, the process is then limited by oxidation and the etching is selective (Fig. 11c). A
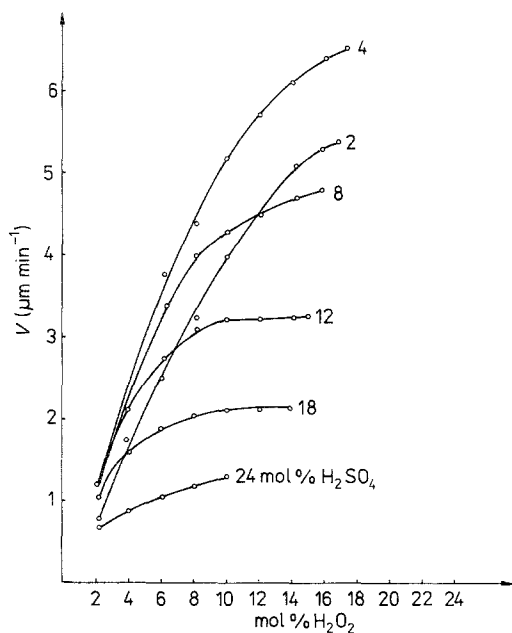

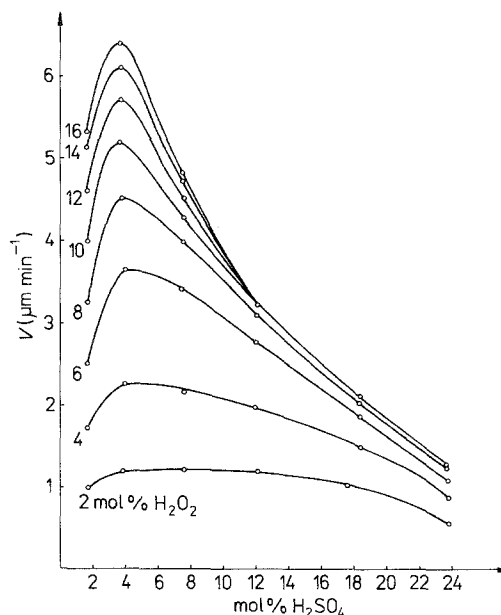*Figure 5* (1 0 0) GaAs etching rate plotted against H_2O_2 concentration. Unstirred solutions.

Figure 6 (1 0 0) GaAs etching rate plotted against H_2SO_4 concentration. Unstirred solutions.
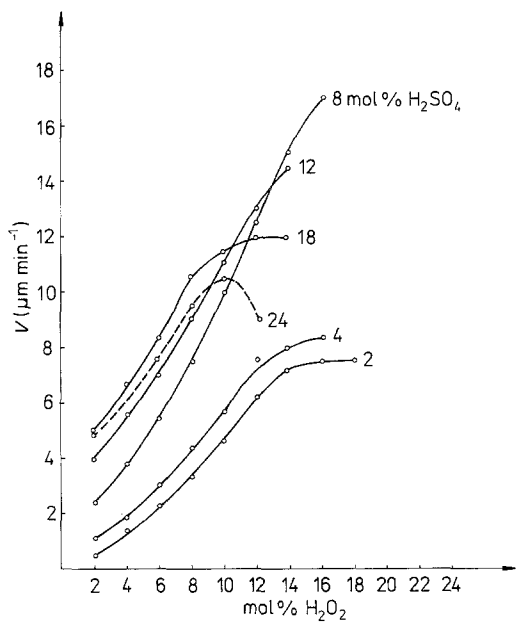
Figure 7 (1 0 0) GaAs etching rate plotted against H_2O_2 concentration. Stirred solutions.

sufficiently high H_2SO_4 concentration differs this range from the field a in Fig. 9

$$V \sim [H_2O_2]^c$$

In unstirred solutions, the increase in H_2SO_4 concentration causes large decrease in etching rate, larger at higher oxidant concentrations (Fig. 6). This is due to a diffusion limiting process. The removal of reaction product from the GaAs surface is too slow, as seen from Fig. 12d. Here the sulphuric acid concentration is fairly high thus the diffusion of etching products from the phase boundary into the solution is essential. The solution viscosity is also of some importance (Fig. 10, field d). The surfaces of the wafers etched without stirring reach a mirror-like state only in a narrow band of the composition triangle, on the meet-
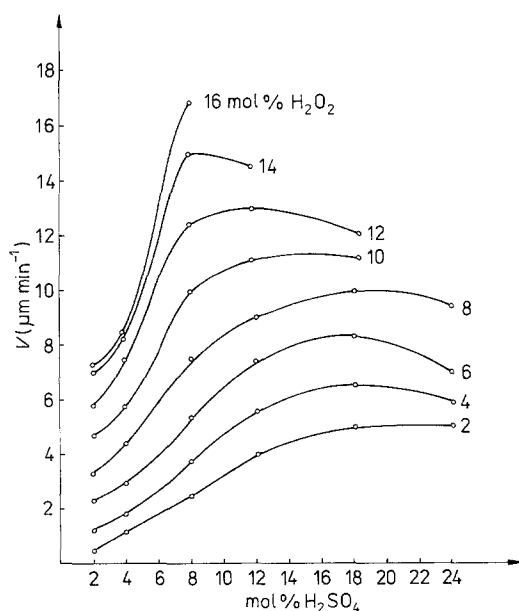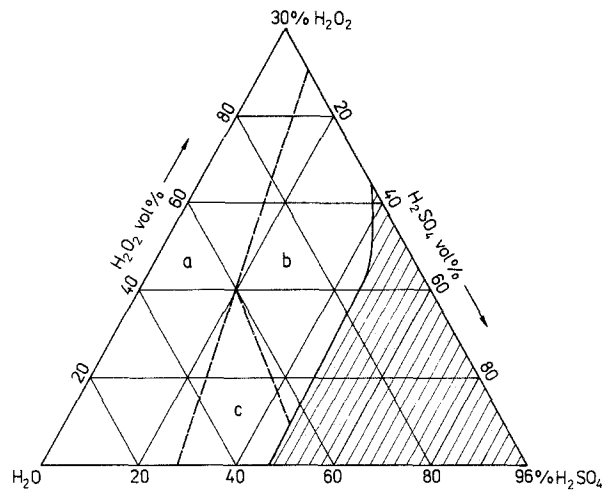

Figure 9 Gibbs' triangle divided into regions of different etching mechanisms and surface types. Stirred solutions. Kinetic limiting agents: (a) selective oxidization of surface at H_2SO_4 deficiency; (b) diffusion of reagents (surface polishing); (c) selective oxidization.

ing point of fields corresponding to different etching mechanisms (Fig. 10 field e, and Fig. 12e). This is not the only case when mirror-like surfaces are obtained in such a composition range where a change of etching mechanism occurs [4]. Field f in Fig. 10 remains in the range of low oxidant concentration so selective etching can be expected and, as a consequence, the surface should develop. In this range, mirror-like surfaces can be observed, but covered with numerous well-shaped crystals, identified as As_2O_3 by X-ray analysis. Weiss [5] also reported that the GaAs $(1\ 1\ 1)_B$ surface is covered with arsenolite crystals. The etching process is limited here by diffusion of H_2O_2 molecules to the solid surface, whereas adsorption and oxidation proceed without any obstacle, probably due to the high
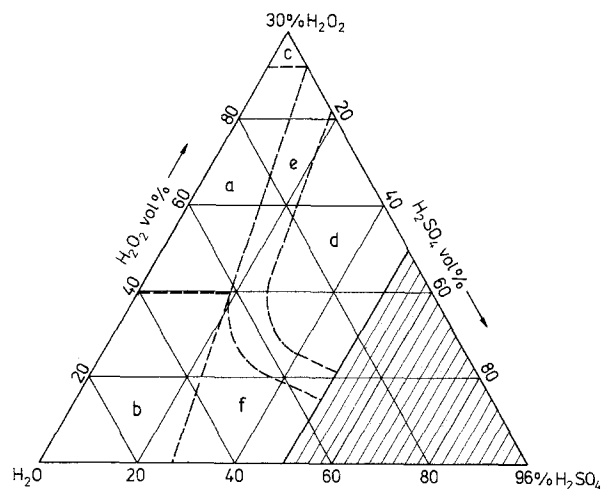

Figure 8 (1 0 0) GaAs etching rate plotted against H_2SO_4 concentration. Sitrred solutions.

Figure 10 Gibbs' triangle divided into regions of different etching mechanisms and surface types. Unstirred solutions. Kinetic limiting agents: (a) selective oxidization of surface at H_2SO_4 deficiency; (b) selective oxidization of surface in dilute solutions; (c) intensive oxidization of surface, deposit occurs; (d) diffusion of products from the phase boundary into the solution, deposition; (e) intermediate range, polishing; (f) oxidization agent diffusion to phase boundary, polishing, deposition.
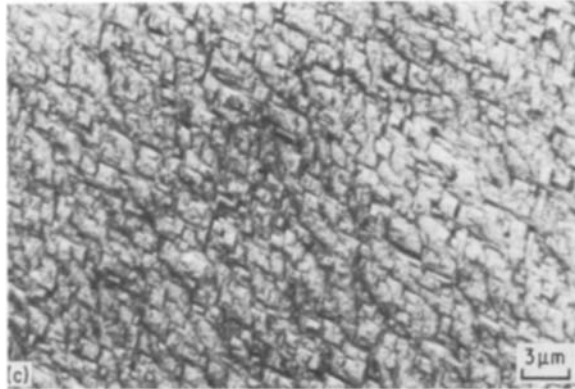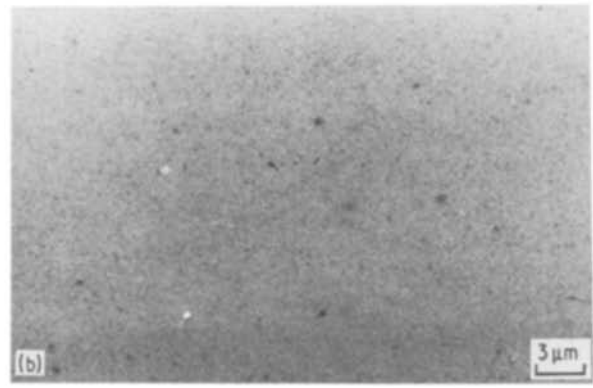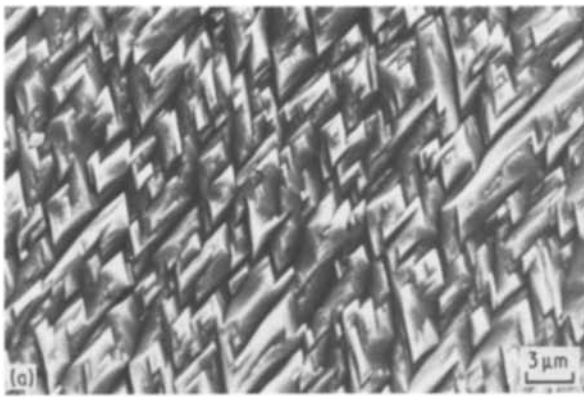
Figure 11 (a, b, c) Scanning electron micrographs of surfaces corresponding to regions indicated in Fig. 9.

H_2SO_4 concentration and the activating role of H^+ ions.

The results presented above, particularly those dealing with the surface state, have no absolute value, especially those obtained during etching in an unstirred solution, because the surface state changes with etching time. Our, results were obtained after etching for some tens of minutes and were reproducible within the accuracy of measurement.

4. Etching profiles

It is interesting to compare the above results of GaAs etching in an H_2SO_4–H_2O_2–H_2O mixture with the shapes of grooves etched in the (1 0 0) surface in various directions. All the grooves were etched without stirring at 21 to 23° C to depths of about $20 \mu m$. We observed a series of grooves etched by solutions with fixed concentrations of oxidant (20 vol % H_2O_2) in the range 20 to 50 vol % H_2SO_4, and another series etched

by the soluion containing a constant concentration of H_2SO_4 (20 vol %) and 20 to 80 vol % H_2O_2.

The shapes of the grooves aligned with [1 $\bar{1}$ 0], [1 0 0] and [0 1 0] did not depend on solution composition. They were V-shaped with (1 1 1)$_A$ limiting surfaces for the grooves aligned with [1 $\bar{1}$ 0] and U-shaped (with round or flat bottom) for both remaining directions. The change in shape of the [1 1 0] aligned grooves is quite interesting, though difficult to explain. These shapes are seen in Fig. 13. With a fixed concentration of H_2SO_4 the increase of oxidant concentration is followed by gradual decay of (1 1 1)$_B$ walls until the bottom becomes rounded. The increase in H_2SO_4 concentration causes the (1 1 1)$_A$ walls to disappear and the profile also becomes round.

The diversity of groove shapes is accounted for by anisotropy, i.e. the different etching rates of exposed surfaces, in particular (1 0 0), (1 1 1)$_A$ and (1 1 1)$_B$. It is also connected with the adhesion of masking material to the wafer surface.

Adachi and co-workers [6–10] reported results of wide investigations of the correlation between the shapes of etched grooves and surface orientation, groove direction and type of solution applied. However, he also could find no simple relation between solution composition and groove shape. An analysis of the masking material and the undercutting influence on groove shape was carried in detail by MacFadyene [3].

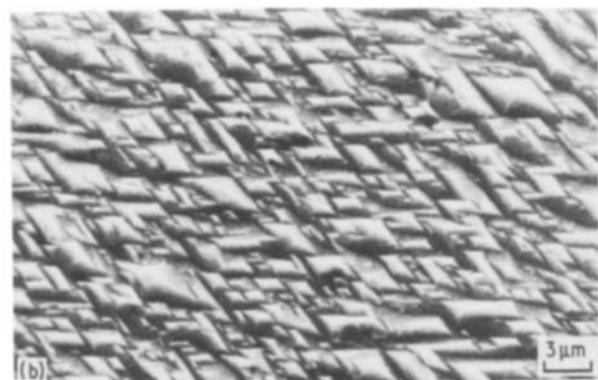The shapes of grooves presented in Fig. 13 are

Figure 12 (a to f) Scanning electron micrographs of surfaces corresponding to regions indicated in Fig. 10.
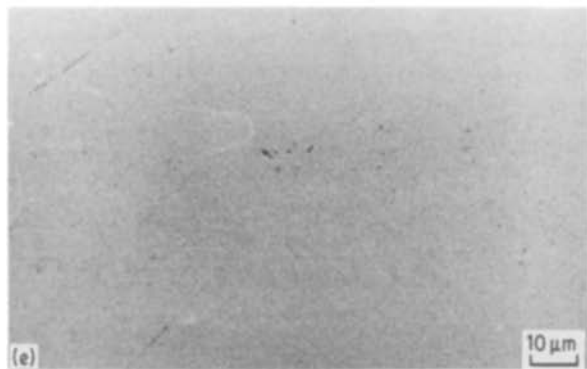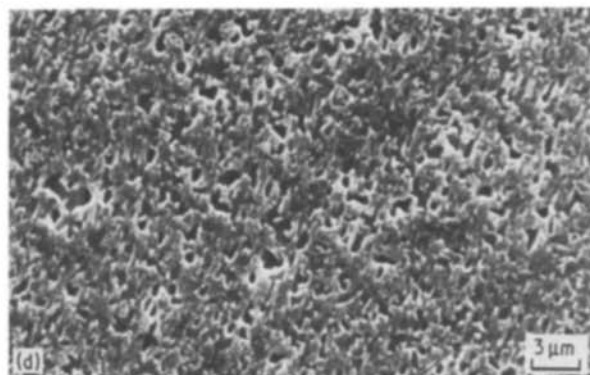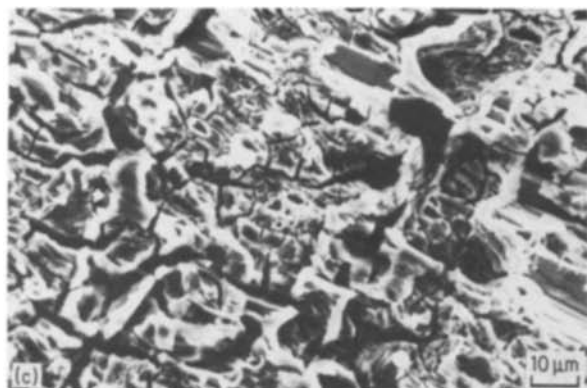
Figure 12 Continued.

consistent with the proposed etching mechanisms assigned to particular regions of the composition triangle (Fig. 10). Whenever the etching proceeds anisotropically (Figs 10a, b and 12a, b) the groove bottoms are clearly defined and are limited by the walls $(1\ 1\ 1)_A$ and $(1\ 1\ 1)_B$. In the range of compositions which give smooth surfaces (Figs 10e, f and 12e, f) the observed profiles are round.

5. Conclusion

The solution stability range at room temperature for

H₂SO₄ [vol%]	H₂O₂ [vol%]	(110)
5		
20		
30	20	
40		
50		
60		
	20	
20	50	
	80	

Figure 13 The intersections of grooves aligned with [1 1 0] on the GaAs (1 0 0) surface, depth $\sim 20\,\mu$m, unstirred solution.

the available compositions in the H_2SO_4–H_2O_2–H_2O system have been evaluated. Examination of the etching process in some 50 solutions with various compositions resulted in the diversification of a couple of surface states including a mirror-like surface in both stirred and unstirred solutions. Correlation of these observations with results of kinetic examination enabled us to propose the predominating mechanism in particular composition ranges.

Both etching character and the type of surface affect the shapes of groove profiles oriented along the [1 1 0] direction. The grooves with round bottoms correspond to smooth surfaces, while in all other cases walls $(1\ 1\ 1)_A$ and $(1\ 1\ 1)_B$ and flat bottoms are revealed.

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