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Chemical etching of (1 0 0) GaAs in the HNO_3-HF-H_2O system

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This paper describes the action of solutions containing nitric acid, hydrofluoric acid and water on GaAs of (1 0 0) orientation. Single-crystal slices of the semiconductor were immersed in the etch and the rate of dissolution was measured. Results were taken over a wide range of composition of the solution. The results show a marked resemblance to the etch-rate data for silicon in the same etching solution, although the actual etching rates for GaAs were lower. The semiconductor surfaces were observed carefully after etching, using techniques of optical microscopy and scanning electron microscopy. Etch hillocks were observed for many compositions of the etch. It was found that the hillocks were covered by a layer of oxide: if any of this oxide covering came off, the hillock quickly disappeared. Sequential etching experiments showed that the hillocks were not associated with dislocations. Both the etch-rate data and the microscopic examination of the GaAs surfaces suggest that the system is probably diffusion-limited over the range of etch composition studied in this work.

1. Introduction

A great variety of liquid solutions has been used for etching and polishing semiconductors, most of them determined by a process of trial and error. A review has recently been published describing some of them [1]. In general, the solutions are based on some strong oxidizing agent such as HNO_3, H_2O_2, or bromine. Of the nitric acid solutions, the ones based on various mixtures of HNO_3, HF and water are among the most commonly used. Extensive work has been carried out to investigate the action of this system on silicon [2–4] and germanium [5]. It has also been used in various compositions to etch GaAs [6, 7], InAs [8] and ZnTe [9]. Very little systematic work has been carried out, however, on the effect of the system on the compound semiconductors. In the work to be described in this paper, (1 0 0) GaAs was etched in HNO_3–HF–H_2O over a wide range of composition, and etching rates were measured at 20° C. In addition, the etched surfaces were carefully inspected using optical and scanning electron microscopes and the surface features were studied.

2. Experimental

GaAs in the form of single-crystal slices of (1 0 0) orientation was used. The slices were about 0.5 mm thick, 0.5 cm^2 in area, and n-type, with carrier concentration in the region of 10^{15} cm^{-3}. They had originally been cut from melt-grown crystals so that in the as-received condition, the material just below the surfaces was damaged from the cutting process. This damaged material was removed by polishing the slices in a 1% solution of bromine in methanol, on a soft polishing pad. A flat, damage-free surface, with virtually no features was produced, giving a good "neutral" surface to start with. A specimen was initially weighed and cleaned before being put into a HNO_3–HF–H_2O solution of known composition. (The reagents used in the work were 40% HF and 40% HNO_3.) The specimen was immersed in 100 cm^3 of the etch and agitated for a measured time. At the end of this time, the etching was arrested by pouring in a large quantity of water. The specimen was then removed, dried and re-weighed to determine the amount of material dissolved. The appearance of the etched surfaces was observed using both

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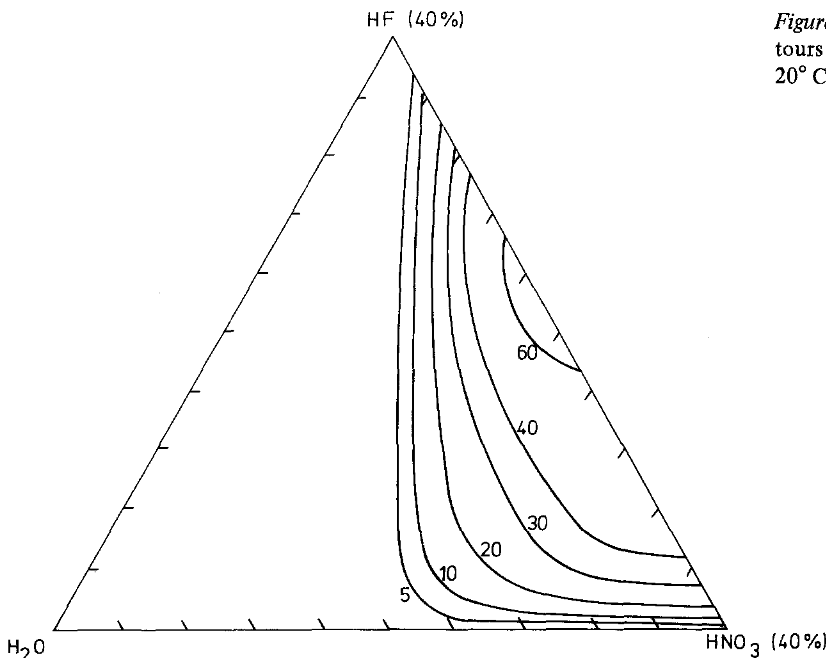

Figure 1 Constant etching rate contours ($\mu m\ min^{-1}$). Data obtained at 20° C.

optical and scanning electron microscopes.

The etching times varied between 10 sec and 1 min. At least three determinations were made of the etching rate for each composition of the etch. Solutions were used which covered the whole range of compositions for which the etching rates were in excess of about 1 $\mu m\ min^{-1}$.

A number of experiments was carried out in which the object was to study the progress of the surface features. In this type of experiment, the sample was subjected to sequential etching, i.e. it was given a series of 10 sec etches. At the end of each etching stage, it was quenched and photographed before re-immersion in a new etch for the next stage. At the end of the sequence of etches, the sample was compared with a specimen which had been etched continuously for the same total time.

3. Results

3.1. Etch rates

Fig. 1 shows the triangular co-ordinate system that was used to represent the composition of the etching system. Each vertex corresponds to 100% of one of the constituents. The figure presents the composition of the etch by volume of the constituents rather than by weight. It must be noted that the HF and HNO_3 vertices represent the stock dilute acids used to make up the solutions. The third vertex represents the amount of added water

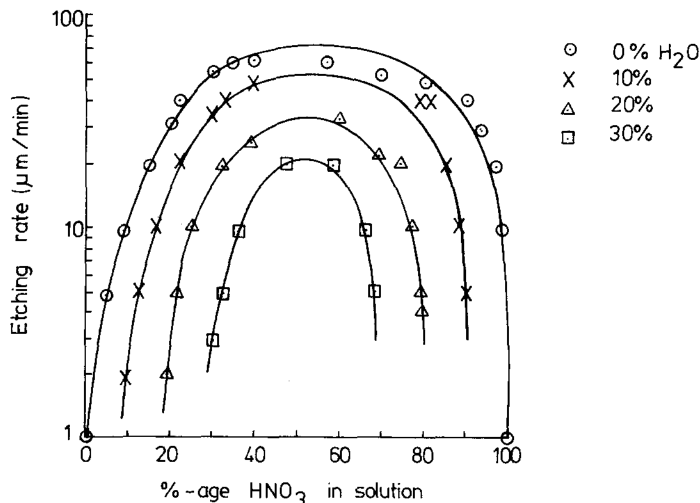

Figure 2 Etching rate as a function of nitric acid concentration for different concentrations of added water.

not, therefore, the total amount of water in the system.

Shown in Fig. 1 are lines of constant etching rate, plotted as a result of a large number of individual determinations. The figure shows several interesting features. At high concentrations of HF, the rate depends on the concentrations of nitric acid and water. This can be seen clearly in Fig. 2, in which the rates are plotted as a function of the percentage of HNO_3 for constant water concentration. A maximum is reached at about 55% HNO_3 for all the curves. To the left of the maxima, the rates are increasing sharply, even though the amount of HF is decreasing. At high concentrations of HNO_3, on the other hand, the constant etching rate contours are lines of uniform HF concentration. The rate remains constant if the concentrations of HNO_3 and water are changed, provided that the HF concentration remains the same. Thus if the data of Fig. 2 are plotted as a function of HF concentration, as in Fig. 3, all the curves coincide as the concentration of hydrofluoric acid approaches 0%.

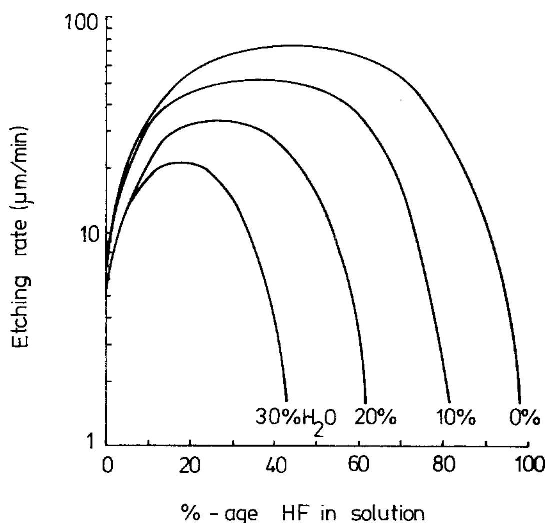

Figure 3 Etching rate as a function of HF concentration for different concentrations of added water.

3.2. Surface features

At the highest etching rates, intense bubbling occurred at the surface during dissolution. This had the effect of sometimes forming "craters", or pock-marks on the polished surface. The most commonly observed features, however, were hillocks. They were seen for a variety of etch compositions, roughly corresponding to etch rates greater than 20 μm min^{-1} in Fig. 1.

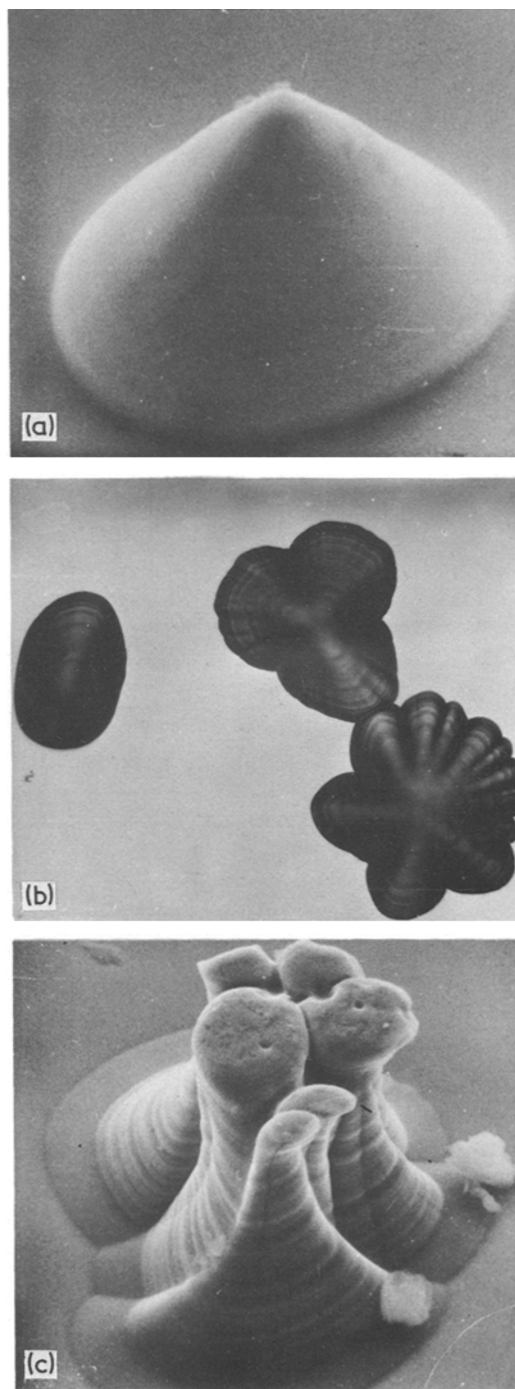

Figure 4 Various hillocks observed on GaAs. (a) "Unit cone", × 2300 (SEM micrograph); (b) most common hillock shapes, × 150 (optical micrograph); (c) unusual hillock, × 1600 (SEM micrograph).

The hillocks were of a variety of shapes. The simplest was the "unit cone" of Fig. 4a. Features of this type were always very small (~1 μm) and were present in smaller concentrations than the

larger hillocks. Fig. 4b shows the more commonly observed types – an oyster-like shape and a multiply curved shape. Occasionally, very unusual forms were seen: one is shown in Fig. 4c. All of the hillocks showed a terracing effect, seen very clearly in Fig. 4b and c as a series of fine lines running parallel to the base of the feature. Both the concentration of hillocks and their average height increased with increasing etching time. If a specimen was etched in $4HNO_3 : 5HF : 1H_2O$ for 10 sec, for instance, the resulting hillocks were normally less then 10 μm high. If the specimen was etched continuously for 50 sec, however, hillocks as high as 60 μm could be found.

The hillocks did not appear to relate to the crystallography of the GaAs in any way. There was no obvious link between the observed shapes and the zinc-blende structure, neither was there any correlation between the way the hillocks lined up on the surface and the underlying (1 0 0) surface of the specimen. This result is in sharp contrast with the hillocks that have been reported on $(\bar{1}\,\bar{1}\,\bar{1})$ InP, for instance [10], for which the sides are precisely-defined (1 0 0) faces, and the features all line up exactly on the crystal surface. Lines were sometimes seen on the GaAs surface on each side of the hillocks (Fig. 5): these were probably due to the flow of etch round the features. If a scratch was made on the surface before etching it was found that a very high density of hillocks was generated along it.

The results of the sequential etching experiments were rather different from the ones involving continuous etching. For the former type of experiment, the density and size of the hillocks were similar after each stage. This meant, for instance, that a specimen etched four times for 10 sec showed hillocks that were smaller and fewer in number than did a specimen etched continuously for 40 sec. A series of 10 sec etches was also carried out in which the same small area of a specimen was observed at each stage. It was found that while the number and size of the hillocks were approximately the same at each stage, they appeared at different points on the surface. The positions that had shown hillocks at the previous stage were still identifiable as rather indistinct scars on the surface. Fig. 6 is a photograph of a specimen showing both new hillocks and the scars from a previous stage. It can be stated, therefore, that the hillocks are not associated with particular points on the surface, but are generated randomly.

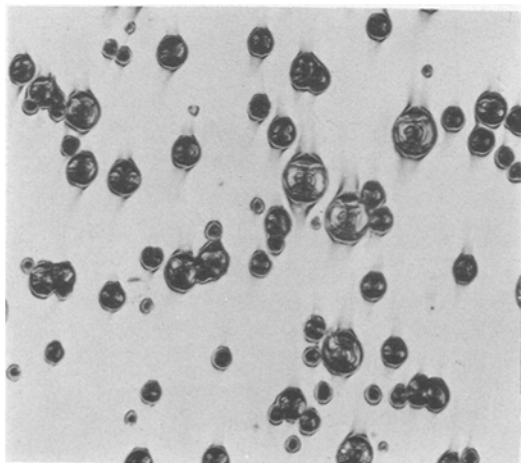

Figure 5 Lines on GaAs surface in the vicinity of hillocks, × 40 (optical micrograph).

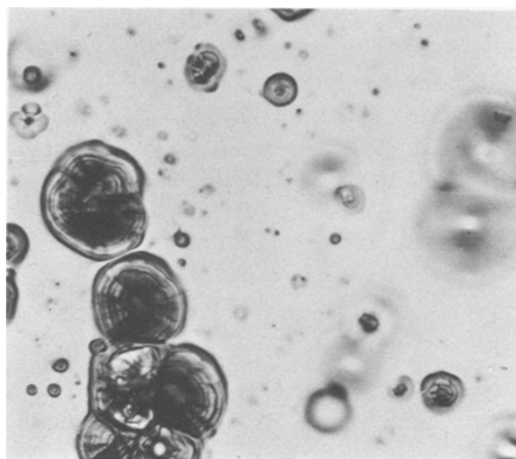

Figure 6 Specimen which had been etched in several 10 sec stages. Both new hillocks and scars of old ones can be seen, × 80 (optical micrograph).

During the sequential etching experiments, hillocks were observed at all stages of development, and it is possible to build up a picture of their life-cycle. Careful observation using the scanning electron microscope showed that they were covered with a protective coating, presumably of oxide. The thickness of the coating increases with etching time until eventually it becomes unstable and cracks appear. Such a situation is illustrated in Fig. 7, in which a portion of the coating has flaked away from the apex of a hillock, revealing the GaAs surface underneath. Note that the GaAs surface is quite smooth, i.e. the terracing is a feature of the coating, not of the semiconductor. In Fig. 8 another hillock is shown

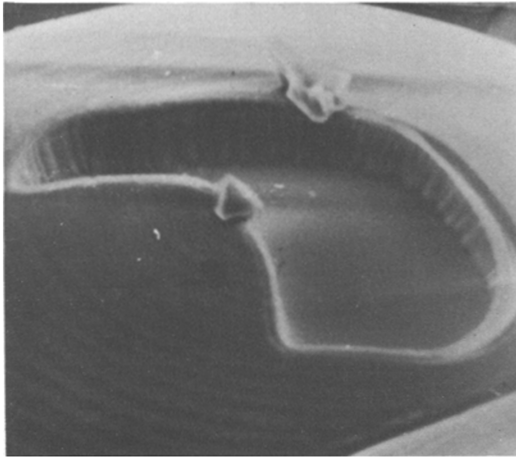

Figure 7 Hillock with part of oxide removed, × 2200 (SEM micrograph).

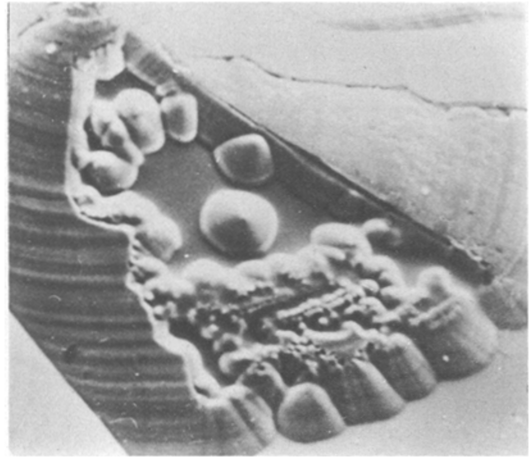

Figure 8 New hillocks nucleating on the side of an old one, × 1500 (SEM micrograph).

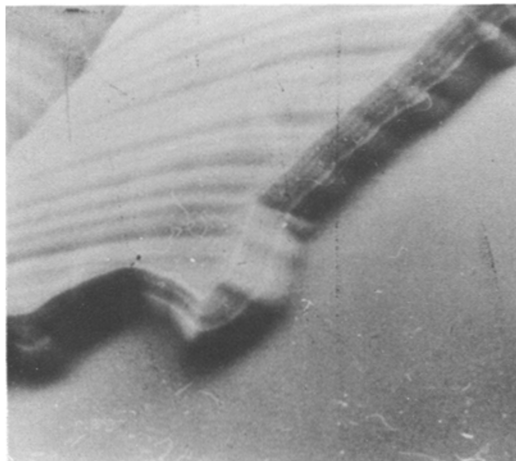

Figure 9 Cross-section of layer, showing layer structure, × 4000 (SEM micrograph).

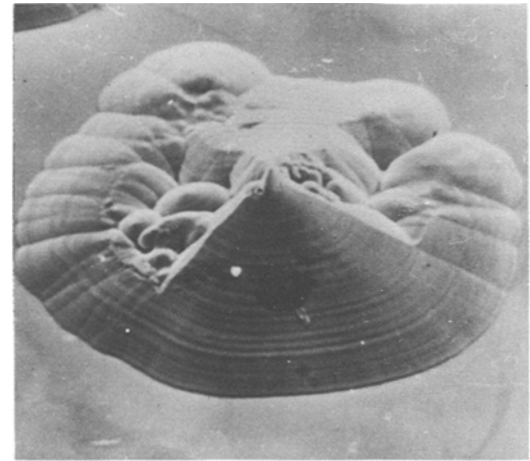

Figure 10 Hillock with re-grown oxide layer, × 750 (SEM micrograph).

in which the crack has developed on the side of the feature. On this specimen, new hillocks have been nucleated on the exposed GaAs surface and another crack is in the process of development, towards the top of the photograph. The oxide coating has a layered structure: this is shown clearly in Fig. 9, which is a cross-section at a crack. The layers have a thickness of the order of 0.1 μm.

Once the GaAs surface has been exposed in this way it can be attacked by the etch. It is likely to disappear at this stage unless a new oxide layer forms very quickly. A hillock is shown in Fig. 10 in which the oxide layer has regrown in time, giving rise to a degenerate, but temporarily stable, feature.

4. Discussion

4.1. Etching rates

When a semiconductor is chemically dissolved in a liquid, a number of processes must occur in series. The observed dissolution rate corresponds to the slowest of these. Molecules of the reacting species must first diffuse through the liquid to the crystal surface. Chemical reactions then occur sometimes in several steps, forming some product. It often happens that this product is not soluble in the liquid, so that further reactions are needed before soluble material is produced. The soluble products then diffuse away from the surface. Many individual processes are, therefore, involved, but it is convenient to divide them into two types;

chemical reaction processes and diffusion processes. The overall etching rate can then be described as being chemically-limited or diffusion-limited, depending on which of the processes is the slower.

It seems likely that the HNO_3–HF–H_2O system acts on GaAs in a diffusion-limited manner, at least over the range of etch compositions studied in this work. One of the features of a chemically-limited system is that it usually etches different crystal planes at different rates. This is because different planes show large variations in chemical activity. The effect is especially marked in the zinc-blende structure. Iida and Ito [11], for instance, showed that for certain compositions of the system H_2SO_4–H_2O_2–H_2O, the $(\bar{1}\,\bar{1}\,\bar{1})$ plane of GaAs etches at five times the rate of the (1 1 1). Other workers have shown similar effects in InSb [12] and InP [10], amongst others. When etching a single plane, this variation of etching rate with orientation ususally reveals itself in the sharply crystallographic nature of any surface features [1]. No such features were observed in this work, as noted in Section 3.2. The hillocks in particular were almost random in shape.

The similarity of the present work with that carried out by Robbins and Schwartz on silicon [2, 3] also suggests diffusion control. In a series of papers, Robbins and Schwartz described in some detail the etching of silicon in the HNO_3–HF–H_2O system. They presented results looking very much like Figs. 1 to 3, although their etching rates were greater. They came to the conclusion that the etching process was diffusion-limited for their experiments, although the details of the chemical process were very complex. It seems likely that the first step in the dissolution is the oxidation of the silicon by products of the nitric acid. This reaction is "autocatalytic", i.e. to some extent self-sustaining, with some of its products being fed back to act as reactants (see [1] for details). The silicon oxide is not soluble in water, but can react with the HF in the system to produce a water-soluble product. This diffuses away from the surface, thereby completing the dissolution process.

GaAs probably etches by a similar sequence of events in HNO_3–HF–H_2O, although is is difficult to be precise because the exact nature of the oxide is not known. Schwartz [13] has reported that $Ga_2O_3 \cdot H_2O$ is a major intermediate in the etching of GaAs in aqueous systems, and also that As_2O_3 can be produced by the action of HNO_3 on GaAs. Kyser and Millea [14] have also reported the formation of As_2O_3 on GaAs after immersion in nitric acid. What is clear from Figs 7 to 10 in this work is that an oxide of some sort is produced on the semiconductor.

Working on the assumption that the etching of GaAs in HNO_3–HF–H_2O follows the same general line as that of silicon, the following commentary can be given on Figs. 1 to 3. To the left of the maximum of Fig. 2, the etch rates depend on the concentrations of HNO_3 and water: the chemical reaction may be autocatalytic. The HF is present in excess, so most of the GaAs surface is stripped of the oxide as soon as it is formed, although small pieces might adhere locally. Beyond the maximum, the balance tilts the other way. As the nitric acid concentration is increased (and the HF concentration is decreased), the HF is unable to remove the oxide immediately and a layer builds up. The dissolution of the oxide then becomes the rate-limiting step, and this depends on the rate at which HF can diffuse to the semiconductor surface. The surface, therefore, becomes dependent on the HF concentration, as shown in Fig. 3. For very low concentrations of HF, the oxide layer becomes thick and passivates the surface, i.e. the etching rate effectively becomes zero.

4.2. Surface features

Reports of the occurrence of etch hillocks on semiconductors are relatively few in number. They have been seen in InP [10], SiC [15] and Ge [16]. These reports all differed from the present work, however, in the sense that the hillocks were "crystallographic", i.e. they had shapes which related to the crystal structure. The most likely explanation for this difference is that the GaAs system is probably diffusion-limited as noted above. The InP and Ge systems are both chemically-limited (the action of the SiC etch is not known).

Batterman, in his work on hillocks formed on Ge by Superoxol [16], found that their formation was not related to internal structure, but was a surface-nucleated phenomenon. A Ge surface kept free of contamination produced relatively few hillocks. For the SiC system, on the other hand, evidence was presented to show the hillocks correspond to the points of emergence of dislocations at the surface. Sequential etching experi-

ments, for instance, showed that the SiC hillocks always appeared at the same points on the surface. This is quite different to the result described in Section 3.2, and the conclusion must be drawn that the GaAs hillocks are not associated with dislocations, but are surface-generated, as with Ge. It is interesting to note, however, that Patel and Mathai [15] reported that the SiC features were terraced in much the same way as those of Fig. 4.

From the evidence of Section 3, the life-cycle of a GaAs hillock would appear to be as follows. An oxide of some sort is produced on the GaAs surface by the HNO_3. This is normally dissolved by the HF and a steady-state occurs, with a constant etching rate. At certain local spots, random effects allow patches of oxide to get thicker than average, passivating small areas on the surface. The region around a spot dissolves away, leaving a hillock. The simplest type is shown in Fig. 4a. The most complicated hillock shapes such as those of Fig. 4b are probably due to several of the simpler hillocks "growing" together. For increasing times of immersion, the oxide layer becomes thicker. The mechanism of oxide growth is not clear: it could be due either to reactants diffusing through the layer and attacking the GaAs underneath, or due to oxide which has been produced in the vicinity of the hillock settling on the outside. In either event, it grows in a very ordered, layered form (Fig. 9).

Eventually the layer becomes unstable and a piece flakes away, revealing the underlying GaAs. Small pieces of the detached oxide often re-attach themselves to the GaAs, either on the uncovered material, or on the surface close to the foot of the hillock. This gives rise to a new generation of hillocks, as shown in Fig. 8. Once the oxide layer has become detached, the hillock usually disappears, however, leaving behind the traces shown in Fig. 6.

It has been proposed that the nucleation of the hillocks is a random process. It would be expected, therefore, that a longer etching time would produce hillocks that were, on the average, larger and more numerous. Both these effects were observed. The result for the sequential etching was different, however. The GaAs surface looked much the same after each 10 sec etching stage no matter how many such stages had been carried out, i.e. the hillocks were of the same size and density. The most likely explanation of this effect is that removal from the etch at the end of a stage damages the oxide layers on the hillocks, probably due to attack by the atmosphere. Existing hillocks are, therefore, destroyed as soon as the specimen is replaced in the etch. Hillocks observed at the end of an etching stage are, therefore only those nucleated during the previous 10 sec.

It was noted in Section 3.2 that a very high density of hillocks was observed at a scratch. At first sight, this might seem to be evidence that they were associated with dislocations. The sequential etching experiments rule out this possibility, however. There is a good deal of evidence to show that most etches act more rapidly at a work-damaged surface [1]. The attack of the HNO_3 on the GaAs in the vicinity of the scratch should, therefore, be more vigorous than elsewhere on the surface. This attack probably gives rise to an excess of oxide which cannot be easily dissolved in the liquid and which, therefore, stays on the surface to nucleate hillocks.

5. Conclusions

The action of the HNO_2–HF–H_2O etch on (1 0 0) GaAs has been studied and the etch-rate data plotted as a function of composition. The results are qualitatively very similar to those found by previous workers who used the same etch for silicon. It seems likely that the etch works in a similar way in both silicon and GaAs, and is diffusion controlled in both cases. Etch hillocks were observed. They do not correspond to points of emergence of dislocations on the surface. They have a protective coating of oxide and if this cracks, the hillock usually disappears. They are nucleated by a random process in which a point on the surface acquires a covering of oxide which is thick enough to cause local passivation.

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