E. W. file

LB-947

A STUDY OF THE ETCHING RATE OF GERMANIUM

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Approved

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Introduction

The treatment of germanium by chemical etching is important in the production of germanium devices and in the preparation of samples for research purposes. Such treatment is also useful in determining the quality and the orientation of germanium samples, different treatments revealing different properties of the material. The treatments themselves, however, have not been well understood. There have been few attempts to explain their behavior, and almost no quantitative data has been collected to show how they do, in fact, behave. The purpose of this bulletin is to provide a useful catalogue of what happens as the conditions of treatment are changed.

General Discussion

Most of this work was done on n-type germanium with an etch consisting of hydrofluoric acid, hydrogen peroxide and water (herein called No. 2 etch). However, comparisons were made in some instances with other compositions and with other etches. One interesting result was a value for the thickness of the disordered layer on germanium due to hand grinding; based on etch-rate evidence, this was found to be from 2 to 10 microns, depending on crystal orientation. Another study determined how the etch rate varied with temperature on different crystal surfaces. It was found that the data did not give a simple straight line when plotted as log rate vs reciprocal temperature (corresponding to a single activation energy). Rather, the slope of the plotted curve decreased as the temperature was increased, with a knee in the vicinity of room temperature. The (110) surface etched most rapidly at all temperatures. Dilution with water reduced the rate of etch linearly with the dilution factor. When either the hydrofluoric acid, or the hydrogen peroxide, concentration was varied, the etch rate varied in proportion at low concentrations but leveled off at high concentrations. Higher purity (9 ohm-centimeter) germanium etched only slightly faster than lower purity (1 ohm-centimeter) and no striking differences were noted due to the type of impurity element. Thermal quenching of a sample also failed to alter the etch rate.

Fast-acting etches such as the No. 3 etch, in which nitric acid is used in place of the hydrogen peroxide, or the No. 4 etch which uses nitric and acetic acids and bromine, were very erratic in performance compared with the No. 2 etch. Some evidence was found that the No. 3 and No. 4 etches fail to react promptly on certain types of germanium surface layers. It is suggested that, if fast etching is desired, greater reliance can be placed on a strong peroxide-hydrofluoric acid etch.

Test Samples

To insure reliable measurements, all samples (except as specifically noted) were cut from the same crystal. This crystal was divided first into "sections", the "sections" into "slabs", and the "slabs" into "pieces". A uniform cutting and numbering system was used, as shown in Fig. 1. As shown in the figure, the designation T312N 4(110)2-1, for

example, would indicate crystal T312N, fourth section, (110) faces, second slab, first piece. Other pieces from the same slab have different suffix numbers. Thin slabs were used so that the contribution of the edge area to the total surface of the pieces would be small. The edge area was included in the total area as if it were of the same orientation as the main surface. The error introduced in this manner was less than 2 per cent.

General Precautions

Since little was known about the effects of various parameters on the etching rate, much effort was devoted to insuring that only the parameter under investigation was influencing the results. This was done either by comparison of samples differing in only one respect or by direct experiment to determine what parameters could safely be ignored.

Temperature: The temperature was maintained constant by immersing the etching vessel in a constant temperature bath. The volume of etchant used (about 50 cc) was large compared to the samples. The temperature of the etchant was measured directly to ± 0.3 degrees C by means of a polyethylene coated thermometer.

Resistivity: The samples used were kept short so that the variation in resistivity along the length was less than ± 5 per cent from the mean except for the 1 ohm-cm sample (next section). To minimize cross-sectional variations of resistivity, which may be present in a grown crystal, samples compared in a given test were selected to be the same distance from the surface of the crystal.

Etch Composition: Etches were made up fresh each day in batches large enough so that the composition was measured with accuracy substantially greater than the assay of the reagents used. Most work was done with the simplest etch (1 HF, 1 H_2O_2, 4 H_2O), called the No. 2 etch (see appendix for etch compositions). The variation in the concentration of the reagent H_2O_2 used (5 parts in 30) was sufficient to introduce a rate error of about ± 4 per cent. However, in most experiments the same reagent was used, so although the absolute values may be affected, the accuracy of the comparisons is determined by other factors.

Faust[1] has reported that the presence of polyethylene in contact with the HF-H_2O_2 etch increases the reaction rate. Both the reagent HF and H_2O_2 in the present study were stored, prior to use, in polyethylene bottles. To determine stability, a stock solution of No. 2 etchant was kept in a polyethylene bottle for an additional six weeks; the rate measured at the end of this period was exactly the same as that measured at the start. This indicates that etching solutions may actually be made up in large quantities and used over a considerable period of time.

[1] J. W. Faust and J. P. McKelvey, Joint IRE-AIEE Conference on Transistor Research, Penn State College, July 6-8, 1953.

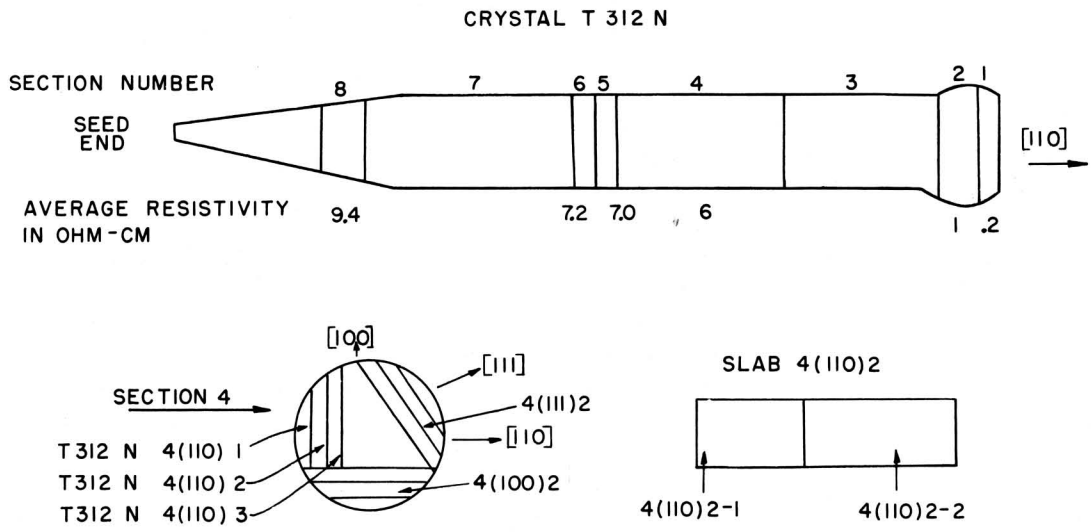

Fig. 1 - Location and numbering of samples for a typical crystal.

Weighing: Etching rates were obtained by measuring the loss of weight of the sample during a fixed time of etch. Weights were measured to ±0.2 mg. The weight differences were usually of the order of 20 mg.

Agitation: In order to make certain that the rate of agitation used did not influence the results, a set of measurements was made of the weight loss of a sample etched under different conditions of agitation. This experiment was done at 40 degrees C, a temperature at which the rate of etching was known to be high. The curve is shown in Fig. 2. The data are corrected for temperature but not for change in surface area. One agitation is a movement to and fro of 1 inch in a beaker containing 40 cc of solution, and it is seen that one to two agitations per second are enough to stabilize the etching rate. All subsequent measurements were made at a rate of 2 to 4 agitations/second, well above the critical region.

Surface Preparation: Most samples were fine-ground with American Optical Company No. 305 abrasive and all were pre-etched for five to twenty minutes in No. 2 etch at room temperature. This was apparently more than sufficient to remove the disordered surface layer, as will be seen in the next section of this bulletin.

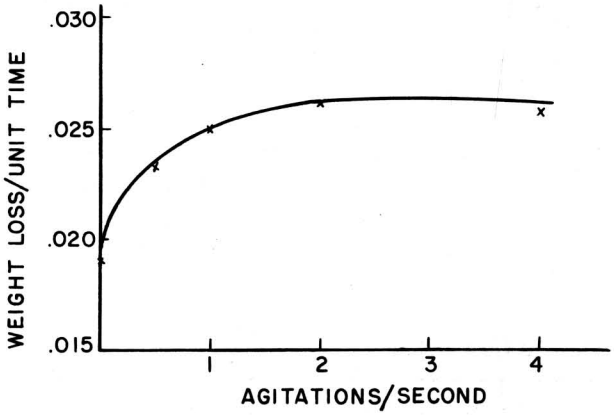

Fig. 2 – Effect of agitation on etching rate.

Rate vs. Time of Etch

A number of thin samples were prepared by uniformly grinding their surfaces with No. 305 abrasive in water on a glass plate. They were weighed, etched for a short time in No. 2 etch at constant temperature, and weighed again. The average rate of etching for this interval was then computed, assuming the normal bulk density of germanium for the surface layers as well. The etching and weighing process was repeated until the rates became constant. The average rates were plotted at the mid points of their respective intervals and a rate-vs-time curve obtained. A representative sample of the experimental results is shown in Fig. 3. The values shown are for three differently oriented samples cut from the same 9 ohm-cm crystal. A second set of data, obtained with 1 to 6 ohm-cm samples, resulted in similar curves, as did data for these samples ground with No. 303½, a coarser abrasive.

If the reasonable assumption is made that the rate of etch becomes constant after the disordered layer has been removed, integration of the curves shows that the depth of the disordered layer is between 2 and 10 microns. This is in good agreement with the value reported by Faust[1] based on lifetime measurements and with that of Weissman[2] based on x-ray line broadening

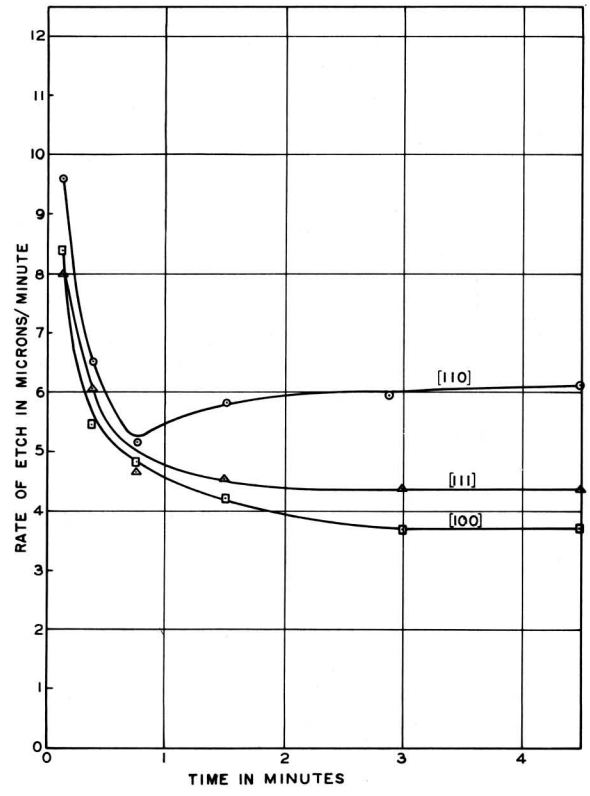

Fig. 3 – Representative rate-of-etch data used in determining depth of disordered layer.

[2] S. Weissman, Rutgers University, Personal Communication.

experiments. However, it is in disagreement with the value 0.5 micron reported by Clarke[3] on the basis of resistivity measurements. Fig. 3 shows that the thickness of the disordered layer depends upon crystal orientation. If the limit of the disordered layer is arbitrarily defined as that point at which the rate has dropped to within 10 per cent of its final value, the calculated results are as shown in Table I.

An explanation which is in fair agreement with the observed facts is as follows: The grinding pits the surface, and the (111) cleavage planes play a prominent role in the pit formation. The basal area of the pits is probably of the same order of magnitude as the cross-sectional area of the grinding particles. The etching process then quickly removes the loose material and starts to lay bare preferred crystal planes in the pits. The rate of etching is dependent upon the particular plane exposed and proportional to the area exposed.

If this explanation is correct, the ground surface itself should show directional properties due to the cleavage faces exposed. This can be observed easily by optical methods. From the cleavage geometry, the depth of the disturbance should be in the ratios predicted in the last line of Table I. The value for the (111) surface will depend on the extent to which the pyramidal pits formed by the (111) planes are truncated by the (111) plane parallel to the surface; thus the range of values shown. It is further required that, as the particle size is increased, the depth of the disordered layer increases and that this depth be of the same order of magnitude as the diameter of the grinding particles. The coarser No. 303½, abrasive is found to give a thicker layer than does the No. 305. The grinding particles were by no means uniform and, of course, changed size as they broke down. However, microscopic examination of the No. 305 abrasive suggests that the larger particles are of the order of 5 microns in their greatest dimension.

[3] E. N. Clarke and R. L. Hopkins, Reported at Joint IRE-AIEE Conference on Transistor Research, Penn State College, July 6-8, 1953.

Rate vs. Temperature for Various Orientations

The temperature dependence of the etching rate was measured for three crystal orientations. The data are plotted in Fig. 4, and it is seen that they do not lie on a simple straight line corresponding to a single activation energy. The points with the dots in the center were taken initially, while those with the crosses in the center are supplementary data taken with the same samples at a later date. The data are fitted approximately by a pair of straight lines which intersect at a knee in the vicinity of room temperature; the mean square deviation from these lines is about 5½ per cent. The slopes of the lines give the approximate activation energies above and below room temperature as shown in Table II.

There are three particularly interesting features of these data; the change in order as the temperature is reduced, the knee occurring in all three curves at about room temperature,

Table I

Thickness of Disordered Layer vs. Crystal Orientation

Sample	Approximate Thickness of the Disordered Layer in Microns, for Surfaces Indicated		
	(100)	(111)	(110)
Set 1. 9 ohm-cm No. 305 Abrasive	7	5	3
Set 2. 1-6 ohm-cm No. 305 Abrasive	5	4	3
Set 2. 1-6 ohm-cm No. 303½ Abrasive	10	10	5
Predicted relative values (see text)	10	0 to 12	5

and the parallelism of the (110) and (111) curves.

Table II

Activation Energy in Kilocalories/Mole

Face	Above Room Temp.	Below Room Temp.
(100)	8.6	13.7
(110)	7.4	12.0
(111)	7.4	12.0

At temperatures above 25 degrees C, the rate is greatest for the (110) face and least for the (111) face. This order is in agreement with the order predicted some time ago from the etching to an equilibrium form of small spheres of germanium.[4] To check the reversal of order of the (100) and (111) faces at low temperatures, two three-faced samples were ground and etched in No. 2 etch to remove the same amount of material. One was etched at 36.5 degrees C and the other at 0 degrees C and the pit shapes were compared. The characteristic pits were different and their shapes tend to confirm the rate data. The fact that the (100) curve is not parallel to the others is strong evidence that the reaction takes place microscopically on at least two different planes.

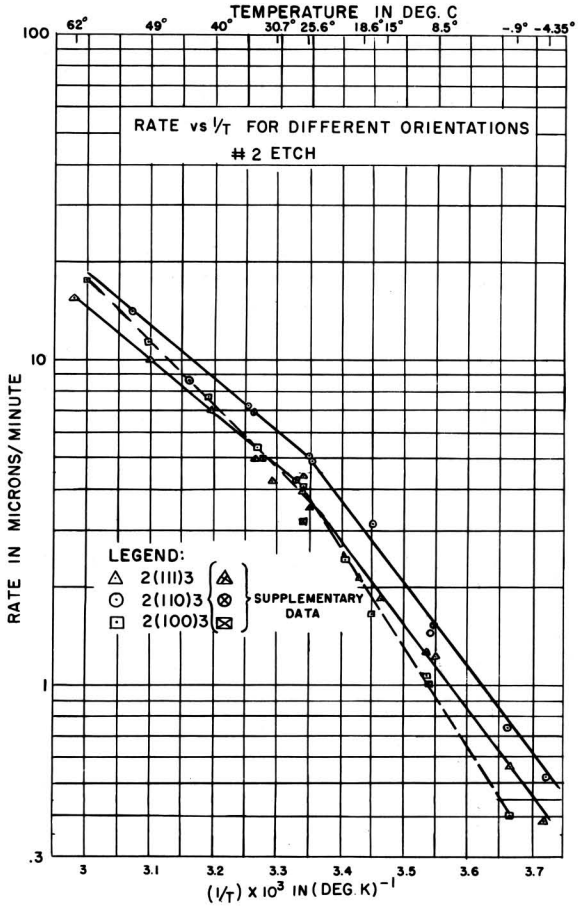

Fig. 4 – Effect of crystallographic orientation on etching rate vs temperature.

The break or knee which occurs in all three curves at about 25 degrees C suggests that the limiting process controlling the rate of the reaction changes at about this temperature. This subject will be considered further in the section on concentration and composition.

The fact that the curves for the (110) and (111) faces are parallel indicates that the temperature dependence of their etch rates is identical. One may then assume that exactly the same process is taking place chemically (the activation energies are identical) but that there is something about the crystal which makes the *a priori* probability for etching the (110) surface slightly greater than that for the (111). Simple arguments based on the relative atom densities in the two planes or on unsaturated bond density do not seem satisfactory.

Concentration and Composition

Much of the lore of etching has stressed the importance of specific composition. Several experiments have been performed to learn how critical this dependence might be. From many preliminary experiments it has been supposed that the reaction involved first the oxidation of the germanium and the subsequent solution of the oxide, but little else was known.

Four sets of data were taken. In one (Fig. 5) the rate-vs-temperature dependence is compared for the standard and a dilute No. 2 etch. The only pronounced effect of dilution was a general lowering of the rate curve. However, it may also be important that the knee of the curve was softened by dilution.

Three sets of data were taken at room temperature but with the composition varied. In Fig. 6 the rate is shown as a function of the strength of the solution for equal proportions of HF and H_2O_2. Over the range covered, the rate dependence is clearly linear.

[4] P. R. Camp, MIT Conference on Physical Electronics, Cambridge, Mass., March 27-29, 1952.

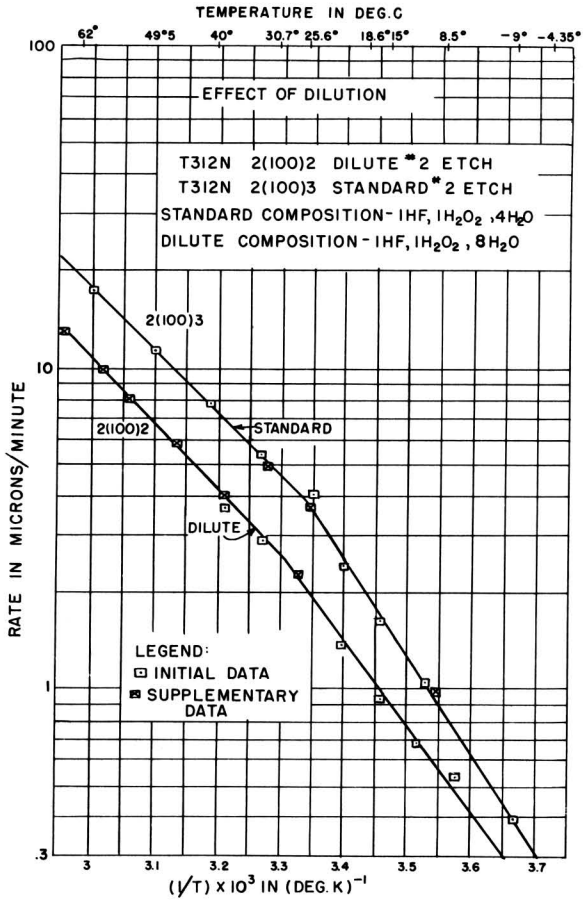

Fig. 5 – Effect of dilution on etching rate vs temperature.

Figs. 7 and 8 show what happens for a (110) surface when either the concentration of the HF or H_2O_2 is held constant and the concentration of the other varied. Both curves are linear in the first portion and then saturate at concentrations not very much greater than that for the normal No. 2 etch. This linear dependence indicates that at some stage in the reaction, each enters as a first order term.

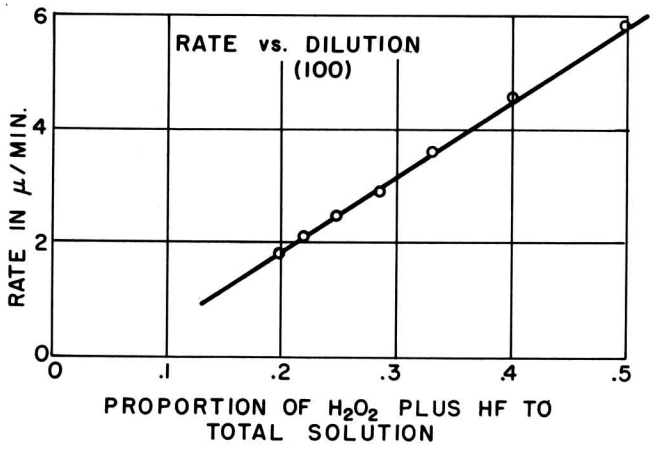

Fig. 6 – Effect on etching rate of diluting etch with water.

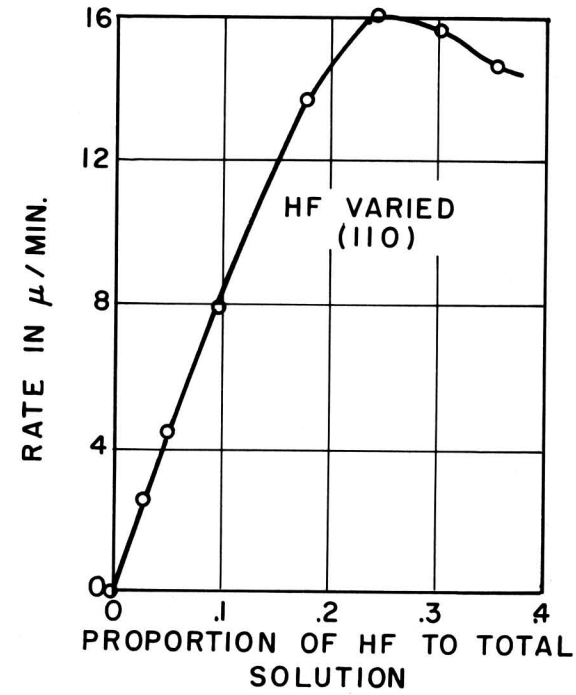

Fig. 7 – Effect on etching rate of varying the HF concentration.

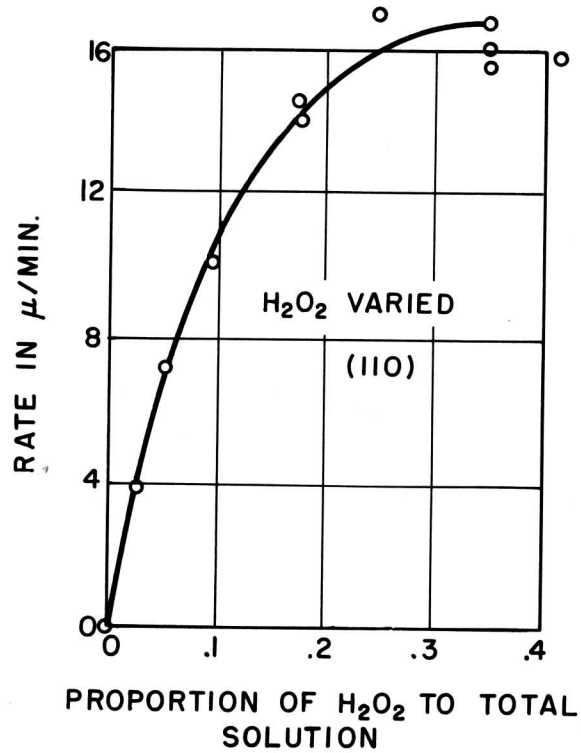

Fig. 8 – Effect on etching rate of varying the H_2O_2 concentration.

The linear dependence on the H_2O_2 concentration also indicates that an early stage of the reaction may be the formation of GeO rather than GeO_2 directly. In comparing Figs. 7 and 8 with Fig. 6, it must be remembered that the crystal orientations are different.

Rate vs. Impurity

To determine to what extent these results could be generalized to apply to other crystals differing in impurity content, three types of measurement were made; the effect of varying the concentration of arsenic, the effect of changing the type of impurity, and the effect of quenching a sample.

Fig. 9 is a plot of the temperature dependence of the rate of etching of a 9.4 ohm-cm sample, (111) surface. Plotted on the same graph are the points for a 1 ohm-cm sample, (111) surface orientation, as a function of temperature and data for (100) and (110) surfaces at one temperature. The single temperature points are the result of more than one observation. Close inspection of the results indicates that the 9 ohm-cm material etches slightly more rapidly (about 10%) than the 1 ohm-cm material. The difference is close to the estimated limit of experimental error but appears to be reproducible. These samples were arsenic doped.

Etching rates have been measured for a number of samples doped with different impurities. The control on these samples was less rigid and as a result, all that can be said is that no striking anomalies were found.

In order to find out quickly the effect of prior thermal treatment on the rate of etch, a simple experiment was tried. Two adjacent (100) slabs were cut from crystal T125N (n-type, 1 ohm-cm, arsenic doped). One of these was heated to a dull red heat in a gas-air flame for about a minute and then quenched by removal. This was repeated three times. The etching rate of the two samples was then compared at 21.8 degrees C and found to be identical to better than the estimated error (2%).

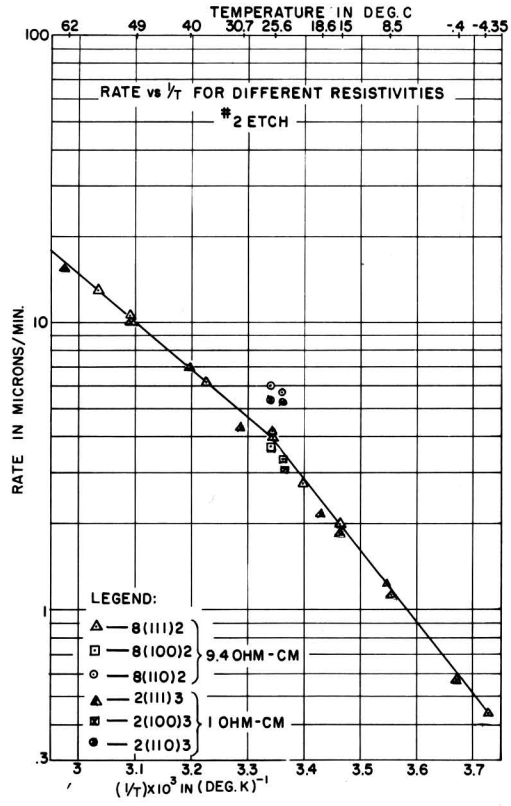

Fig. 9 - Effect of sample resistivity on etching vs temperature.

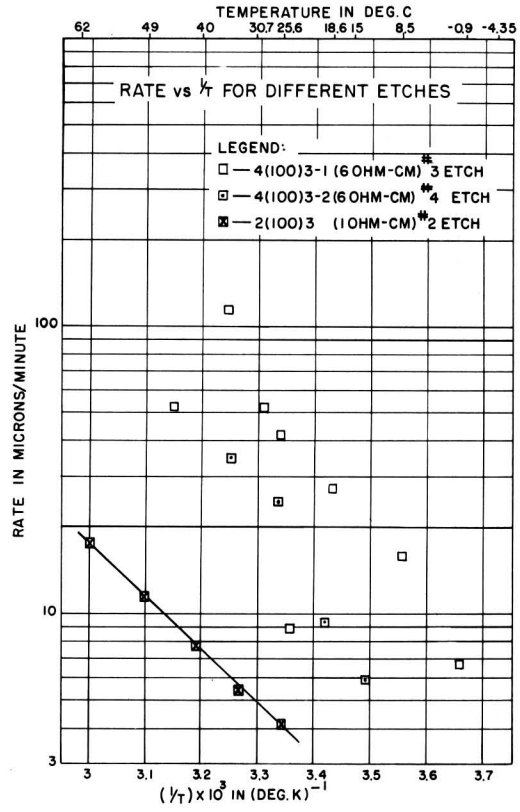

Fig. 10 - Comparison of etching rates for different etches.

Comparison of Etches

Many different etches are used in practice. Some of the most common are listed in the Appendix. The rate-vs-temperature dependence of the No. 2, No. 3 and No. 4 etches have been studied. Some results are plotted in Fig. 10. The data for the No. 3 etch are very erratic and the data for the No. 4 etch are even worse, so that no curve can be drawn. Some of the experiments performed in obtaining these data suggest that sometimes there is formed on the surface of the germanium a layer which acts to passivate or otherwise inhibit the reaction in these etches. For example, a brief etch in No. 2 will make the sample almost immune for a time (a minute or more) to the action of the No. 3 etch. No such inhibiting action has been observed in using the No. 2 etch alone. It follows that it may be desirable to use a concentrated version of the No. 2 etch for the operations in which the No. 3 or No. 4 etch is normally used. An idea of the rates obtainable may be derived from the rate-vs-dilution curve, Fig. 6. An undiluted mixture of reagent H_2O and HF gives a rapid etch.

Paul R. Camp

Appendix

Composition of Commonly Used Germanium Etches

H_2O_2 Technical Quality (Allied Chemical Co.) Assay 30-35%
HNO_3 Reagent Quality (Baker) Minimum Assay 69.2%
HF Reagent Quality (Allied Chemical Co.) Minimum Assay 48%
CH_3COOH Reagent Quality (Merck) Minimum Assay 99.8%

No. 1:
- 2 cc HNO_3
- 4 cc HF
- 4 cc H_2O
- 200 mg $CuNO_3$

No. 2:
- 1 part HF
- 1 part H_2O_2
- 4 parts H_2O

No. 3:
- 56 cc HF
- 56 cc HNO_3
- 12.5 cc H_2O

No. 4:
- 50 cc HNO_3
- 30 cc CH_3COOH
- 30 cc HF
- 0.6 cc Br

Silver Etch:
- 40 cc HF
- 20 cc HNO_3
- 40 cc H_2O
- 2 gm $AgNO_3$