E.W. file

LB-948

MICROSCOPIC EXAMINATION OF GERMANIUM CRYSTALS AND TRANSISTORS

RADIO CORPORATION OF AMERICA
RCA LABORATORIES DIVISION
INDUSTRY SERVICE LABORATORY

RADIO CORPORATION OF AMERICA

RCA LABORATORIES DIVISION

INDUSTRY SERVICE LABORATORY

LB-948

Microscopic Examination of Germanium Crystals and Transistors

Approved

Stuart W. Seeley

Microscopic Examination of Germanium Crystals and Transistors

Introduction

This bulletin discusses the techniques which may be employed in the microscopy of germanium crystals, and the information which may be obtained by the examination of such crystals and of transistors which are made from them. Microscopy is valuable as a supplementary method of examination since it permits a point-by-point study whereas most other methods, such as electrical, mechanical, or thermal methods yield volume-average results.

Useful information may be obtained regarding crystal orientation, twinning, junctions, defects and dislocations, small angle grain boundaries, and the external and internal structure of transistors.

Microscopy

To study crystal orientation, twinning, the shape of junctions and certain crystal defects in germanium by means of the microscope it is necessary to cut, grind (and sometimes polish) and etch the specimen. Germanium, as it is used in semiconductor devices, is much easier to examine under the microscope than is steel, for example. This is because it is a single element, in a very pure state, and the crystals, usually single, have a high degree of perfection. As a consequence, the etching techniques are relatively simple and the crystal defects are often far enough apart to be resolved by the light microscope.

It is too often assumed that on looking through a microscope one sees the specimen--magnified. Actually one sees a magnified *image* produced under very special conditions of illumination. The appearance of this image can be changed widely by changing the illumination. If the illumination is not correctly chosen important information may be completely absent. One consequence of the variation in the image with changes in the illumination is that a photo-micrograph of a germanium surface can convey very little information unless the conditions of illumination are very precisely described. A photo-micrograph is usually meaningful only to the man who takes it. It serves as a memorandum on what he has seen. This is one reason why no photo-micrographs are shown in this bulletin. Instead a plan drawing of the observed structure is given. Beneath this is a sectional elevation of the structure as deduced from the behavior of the image as the specimen and the illumination are manipulated.

Germanium surfaces are most readily

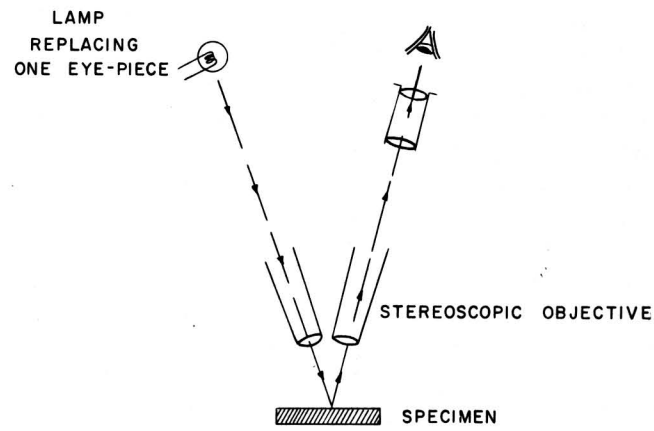


Fig. 1 - Illuminating the specimen through one tube of a stereoscopic microscope.

examined when they are nearly flat, when the normal to the surface passes close to the center of the objective, and when the illumination is normal to the surface. This may be called the bright field condition. When using a low power (x15 to x90) stereoscopic microscope this condition can be achieved, at least approximately, by removing one eye piece and directing light down this tube of the instrument, as shown in Fig. 1. The specimen is then positioned to reflect light into the other objective. Vertical illumination is standard on the metallurgical microscope (x50 to x600) and can be achieved at low power on the Leitz Panphot microscope by the use of an auxiliary mirror as shown in Fig. 2.

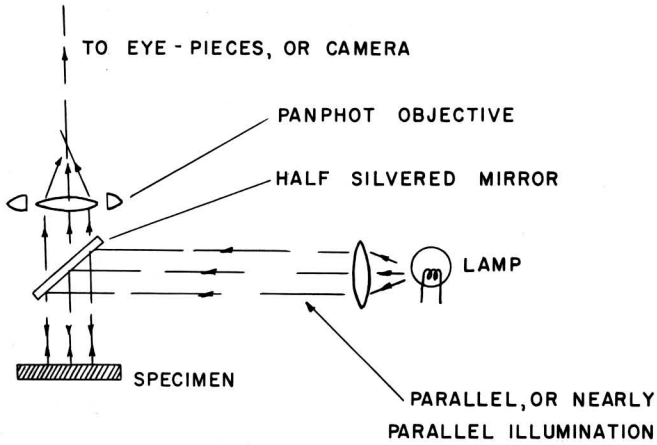


Fig. 2 – Leitz Panphot microscope with an auxiliary mirror to illuminate the specimen.

If the normal to the germanium surface passes near the center of the objective but if the illumination is oblique so that the specularly reflected light does not enter the objective we have the dark field condition. This is achieved with the stereoscopic and metallurgical microscopes by the use of an auxiliary illuminator as shown in Fig. 3. It is standard on the Leitz Panphot microscope, where it is achieved in the manner indicated in Fig. 4. Under dark field conditions the surface is seen, if it is seen at all, because of light scattering. This method of illumination provides a sensitive method for detecting and examining dirt, contamination, and corrosion on the germanium surface. It is a very poor method of examining the germanium itself, however. When a stereoscopic microscope is used with oblique illumination, some parts of the

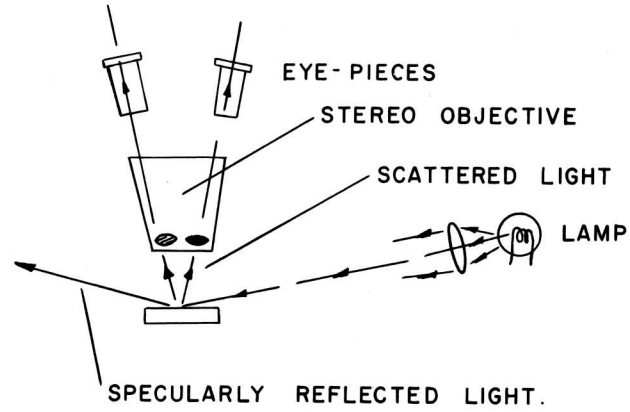


Fig. 3 – Auxiliary illuminator for dark-field studies with stereoscopic microscope.

specimen surface may reflect light into one objective and others may not, so that mixed light and dark field conditions are obtained. At times it may be preferable to use only one side of the microscope to simplify the interpretation of the image.

Oblique illumination is valuable in studying surface shape. Consider the surface ABCD shown in section in Fig. 5. When in the position shown, the whole surface is seen under dark field conditions. If now the surface is rotated counter-clockwise about B, the regions AB and CD will first appear bright because they reflect light into the objective while BC will still appear dark. It can be deduced therefore that the surface AB is higher than the surface

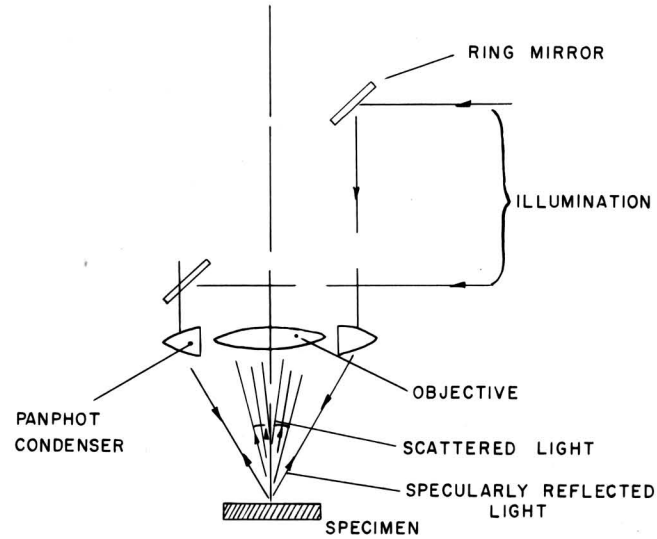


Fig. 4 – Dark field illumination, Leitz Panphot microscope.

CD. This is a very sensitive method. It is particularly useful when the length of BC is large enough, or its inclination to AB small enough, that the difference in focus between AB and CD is difficult to determine.

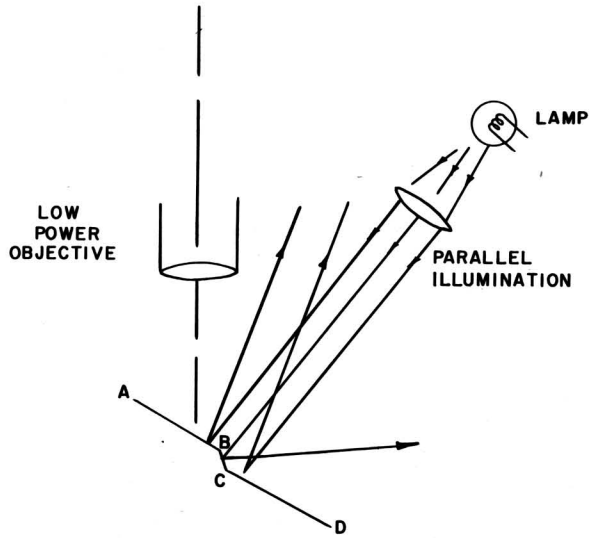


Fig. 5 – Oblique illumination.

Under vertical illumination the following factors help in determining the surface structure. With wide aperture illumination and consequently small depth of focus one can focus on the higher and lower levels of the surface separately, provided that the difference in level is greater than approximately 5×10^{-5} cms. For small structures it may help to remember that concavities turn from dark to light on racking up *through* focus. Convexities give the opposite behavior. On racking up from tilted regions a bright reflection will move across the field. Consider the surface shown in section in Fig. 6. On racking up so that the plane on which the microscope is focused moves from PQ to RS, the reflection from AD moves to CE, and of course goes somewhat out of focus. If the height AB is measured by the fine focus knob, and BC with an eye piece scale θ can be determined roughly from the relation:

$$\theta = \tfrac{1}{2} \tan^{-1} (BC/BA)$$

VERTICAL ILLUMINATION

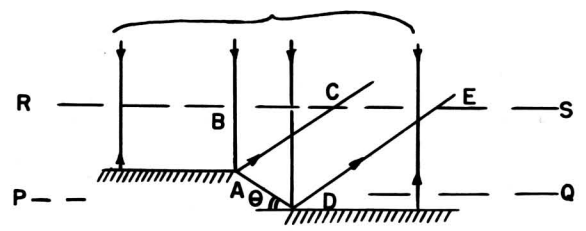


Fig. 6 – Surface structure determination.

Since many examinations require that the germanium crystal be tilted until a certain plane is perpendicular to the axis of the microscope, it is convenient to have a stage which will permit this manipulation. Such a stage is shown in Fig. 7. The test for correct orientation is first brilliance of reflection from the surface under study, and then more critically that details in the surface go out of focus symmetrically on racking up (i.e., do not show a sideways displacement).

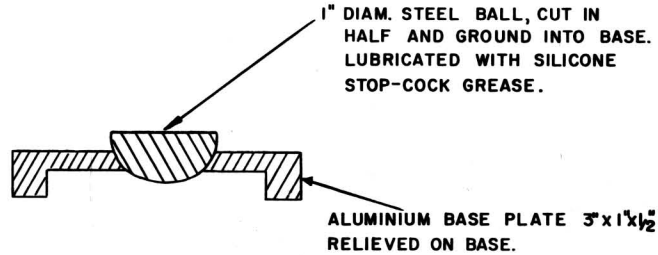


Fig. 7 – Tilting stage for light microscope.

The following techniques and instruments, while not widely available, may be of value in special cases.

Interference Microscopy: Using monochromatic light at vertical incidence one observes the interference fringes formed between the germanium surface and a silvered flat placed close to it. This is a powerful method of detecting and measuring small differences in height on the surface.

Polarizing Microscope: This has proved of little value in studying germanium, though it has in special cases shown some optically active solids on germanium surfaces. The solids could not be identified.

Electron Microscope: One looks not at germanium but at a replica of the surface. The technique being less direct is therefore slower but it is the only one which will give higher resolution than the light microscope. It is wise to precede electron microscope studies by careful light microscope studies.

Specimen Preparation

The crystal is first cut approximately parallel to one of the simpler sets of planes: (100), (110), or (111). It may then be ground on a glass plate using a water slurry of American Optical Co. Nos. 303½, and 305 polishing powders in succession, the plate and crystal being carefully washed before proceeding to the finer powder. In general a high polish is not required.

If much work of this character is anticipated it is worthwhile to use a glass polishing wheel. If the surfaces to be ground are small, the crystal should either be held in a jig or embedded in plastic, so that the ground surface is plane.

The etches in general use in device work, while not necessarily the best for microscopy, are at least suitable and are in ready supply. Their compositions are given in Appendix I. The mode of attack of some of these etches has also been studied and is reported in *LB-947, A Study of the Etching Rate of Germanium.*

Number 2 etch is the most versatile. It should be agitated and used in sufficient volume that its temperature does not rise excessively during use. After its use for 30 seconds to a minute, the orientation of a ground surface can be determined. To study the bulk properties it is often better to pre-etch with the faster number 1 etch until the disordered surface is removed*. This process can be checked with the microscope since when the undisturbed bulk is reached the number 2 etch will produce many fewer pits.

Number 2 etch, particularly if old, may leave a visible film on the germanium surface. This can be avoided by increasing the H_2O_2 concentration. It is preferable to do this just before the etch is used since the H_2O_2 is unstable at room temperature. 30 cc of H_2O_2 added to the above formula is sufficient. A sufficient volume of the etch should be used so that it does not weaken appreciable during the reaction. The test for this condition is that the pit shape does not change on a further short etch with fresh solution.

*X-ray studies by S. Weissman at Rutgers University show that the disordered layer, for purposes of the present report, can be somewhat thicker than the 2 to 10 microns found by etch-rate techniques in *LB-947*. It is suggested that from 25 to 50 microns (i.e., one to two mils) be removed to give a margin of safety.

The number 1 etch is preferable when studying dislocations that terminate on the (100) surface. Number 3 etch when used on a polished surface will show p-n junctions.

Observation of Crystals

Orientation

To check the orientation of a surface it is convenient to start with it in a fine-ground state. It should then be etched in number 2 etch with agitation for approximately 45 seconds. It should be examined at x90 or higher magnification, x300 to x600 is preferable, using vertical illumination.

If the surface is close to one of the major planes it will show one of the pit structures sketched in Appendix II. In the early stages of etching, the pits will be closely packed together. Structures which are ambiguous by the criteria of Appendix II indicate inaccurate orientations. Where the orientation is important such crystals should be recut using an X-ray diffraction examination to determine the plane of the cut.

In this, as in all light microscope observations, the information obtained pertains only to the observed surface of the crystal. Only in the absence of twinning and polycrystallinity can it be assumed to apply to the bulk of the crystal.

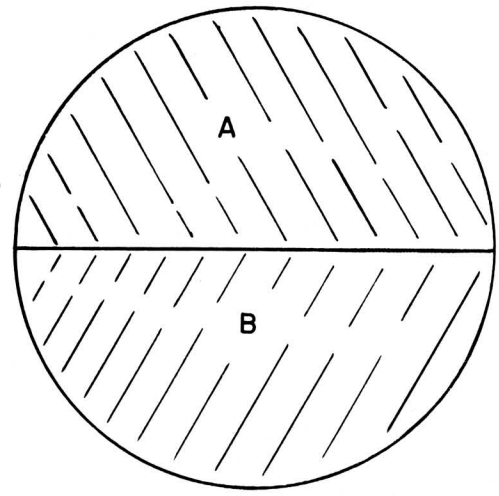


Fig. 8 – A-B twin.

Twinning

The unambiguous proof of twinning by the use of the light microscope is difficult and laborious. A better method involves taking a back reflection Laue pattern with the X-ray beam bisected by the suspected twin plane.

Twinning is nevertheless a sufficiently common occurrence that the observer should be familiar with its appearance. Germanium twins on the (111) plane, one twin being rotated 60 degrees about the [111] direction with respect to the other. The simplest case, an A-B twin is shown in Fig. 8. Twinning is often multiple. The next simplest case an A-B-A twin is shown in Fig. 9. It can be shown from the geometry of the germanium lattice that the part A can form a continuous single crystal, but that if the part B terminates as at PQ, then PQ cannot be a twin plane and will in general be the site of defects. During crystal growth the defects at PQ may nucleate other crystals, making the specimen polycrystalline.

With the crystal prepared as for orientation studies, an AB twin appears as a straight line, or trough, separating two regions of different orientation. If the (111) twin plane is not perpendicular to the surface under examination the surfaces A and B will usually etch to different depths. An A-B-A twin may cause confusion if the B region is so narrow that it cannot be resolved in the microscope. The identification of twins is usually aided by their very specific orientation and by the fact that the twin plane often (though not always) runs for a long distance through the crystal.

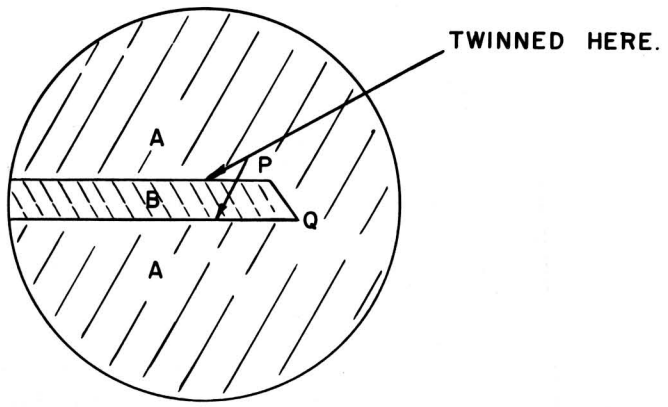


Fig. 9 - A-B-A twin ending at PQ.

Since twinning and slip both occur on (111) planes there is some danger of confusing the two conditions. Slip lines are only seen on *unetched* surfaces, they are moreover softer in appearance and usually less extensive in length than twin lines on a surface. They are discussed further below.

Impurity Effects

Resistivity striations, such as those which have already been described[1], also cause irregular etching on longitudinal cuts on crystals. This is mentioned not as a method for studying such striations (the pulse plating method of *LB-896* is superior) but because it is a possible source of ambiguity in studying the irregular etching figures produced by dislocation arrays.

The position is further complicated by the fact that dislocations and impurities may be expected to interact in the crystal, locking each other in place. It is probable that this interaction is relatively weaker in valence crystals than in metals.

Junctions

One method of delineating junctions, involving differential electroplating, has been described in the literature[2]. In another method[3], the crystal is cut, ground, and polished. The polishing can be done on a glass plate using a water slurry of Linde A powder, or on 4/0 paper using cutting oil, or if the crystal is small and is embedded in plastic the early polishing may be done on polishing paper, the operation being finished with a pad of paper towel and wet Linde A powder. Next, using a camel-hair brush the polished surface is vigorously swabbed with number 3 etch for about 30 seconds. Near the junction the n-type region etches faster than the p-type region.

The examination is best carried out with a low power stereoscopic microscope using parallel illumination. The mixed dark- and light-field condition described in connection with Fig. 5

[1] *LB-896, Resistivity Striations in Single-Crystal Germanium.*

[2] E. Billig and J. J. Dowd, "P-N Junction Revealed by Electrolytic Etching"; *Nature*, Vol. 172, p. 115, 1953.

[3] *LB-860, The Preparation of Single and Multiple P-N Junctions in Single Crystals of Germanium.* A photograph of an etched junction is shown in this report, but the etching procedure is not described in detail.

is employed. In that Figure, AB would correspond to the p-type region.

Defects and Dislocations

The subject of defects and dislocations in single crystals has been reviewed by Seitz[4] and Cottrell[5]. It is probable that, in those etching reactions which are not self-catalytic, each pit nucleates at a defect. Some pits are known to nucleate at disloçations. It does not follow that an observation of the pits, however, will lead to an unambiguous picture of the distribution of dislocations.

Since a mechanically-worked surface has had many dislocations formed in it - the preponderance probably being screw dislocations, it is necessary to etch deeply before attempting to study the distribution of defects in the bulk crystal. Number 2 etch may be used on (111) and (110) surfaces. Number 1 etch is preferred on (100) surfaces. For the interpretation see Appendix II. It should be remembered that, while defects are localized, dislocations are extended. The point of intersection of the dislocation with the surface may move due to jogs as the etching proceeds. This is believed to cause the "terraces" in the terraced pits.

On (100) surfaces it is not uncommon to find the dislocations arrayed in lines. These are small angle grain boundaries - or mosaic boundaries. When the pits are very close (i.e., less than 10^{-4} cm apart) they become difficult, if not impossible, to resolve. One then sees only an etched line, often curved, and usually terminating within the crystal. On surfaces other than (100) and (111), dislocation arrays may etch proud - i.e., be left above the surrounding surface. This same behavior is seen on (110) surfaces.

Proud etching is not an unambiguous sign of dislocations since it may also be caused by impurity concentration (see above).

Dislocations may be caused by slip, by excessive impurity concentration where the solute atoms are misfits, by the termination of twin planes within the crystal, and may be formed during crystal growth particularly wit crystals grown in the [100] direction.

Slip Lines

At temperatures above 600 degrees C, germanium slips on the (111) planes. The intersection of these regions of slip with the free surface of the crystal produces very small steps which are called slip lines. With practice they can be distinguished from twin lines by their appearance. A safer procedure is to etch the crystal. Twin lines are intensified while slip lines disappear usually being replaced by dislocation pits or small angle grain boundaries the corresponding substructures having been formed as a result of the slipping.

Slip lines are best seen under vertical illumination.

Wafers and Bars

Wafers and bars cut preparatory to making devices may be examined by the above techniques for orientation, twinning, junctions, and small angle grain boundaries.

In addition to the appearances described above there will often be found irregula mounds and hollows. Some of these are due to the fact that the germanium was not flat when the last layers of worked material were etched off. These irregularities persist in reduced form on further etching. There are other irregularities which cannot be explained on this basis. Those which persist with little change of shape on further etching are probably due to structural faults in the crystal - arrays of dislocations, inhomogeneities in impurity distribution or both together.

Observations of Transistors

This section will be concerned with the examination of unpotted, alloy junction, p-n-p transistors, using indium or indium-germanium as the alloying material. A cross-section o such a transistor, not typical, is shown in Fig. 10.

An examination of the transistor as received will show the spread of the dots, their alignment (using a stereoscopic microscope t look at the transistor in profile), and whethe

[4] F. Seitz, "Imperfections in Nearly-Perfect Crystals", (W. Shockley, Editor), John Wiley & Sons, N. Y.; p. 3, 1952.

[5] A. H. Cottrell, "Progress in Metal Physics, (B. Chalmers, Editor), Interscience Publishers, N. Y.; Vol. I, p. 77, 1949; Vol. 4, p. 205, 1953.

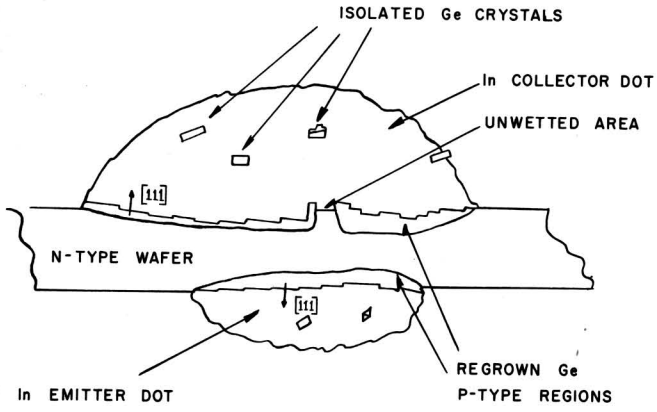


Fig. 10 - Cross-section of Indium-on-Germanium p-n-p transistor.

or not the final etching has been done. This last can be judged by the extent to which the isolated germanium crystals in the dots can be seen. A dark-field examination will also indicate the cleanliness of the surfaces of the wafer.

In the next step the indium dots are removed using an etch which does not attack germanium. This may be concentrated hydrochloric acid or mercury. Mercury is faster but must be cleaned from the transistor by a dip in nitric acid. The nitric acid dip should be a short one since nitric acid slowly attacks germanium. The germanium crystals which had previously been isolated in the indium dot may now be washed away and the wafer dried.

The region of recrystallization should now be observed under vertical illumination (if the wafer surfaces are nearly (111) planes). With the wafer tilted to give the maximum reflection from the regrowth crystals the [111] direction coincides with the axis of the microscope. Hence the departure of the wafer from the horizontal measures its misalignment from the [111] direction. Unwetted regions can usually be detected by the misalignment of the surface with the [111] direction, but even when the orientation is good, it will be seen that the unwetted germanium has a different surface texture from that of the regrowth crystals. This surface texture is the same as that found outside the region of the dots. Sometimes the regrowth crystals will form a cap over an unwetted region. In such cases the regrowth crystals must extend above the general surface of the wafer. Judicious probing with a needle will test such cases.

A crude examination of the junction can sometimes be made by breaking the wafer so that the fracture surface crosses the dot regions. Such fracture surfaces are seldom flat enough to permit careful study. A better method is to embed the wafer in Bioplastic or Araldite being careful to exclude air bubbles so that the wafer is well supported. It may then be cut, or ground down to a suitable cross-section, polished on 4/0 paper with oil, and etched to show the junctions.

Examination under the microscope will now show the junction shapes, the variation of base thickness between the junctions, and the thickness of the regrowth regions. This information, of course, pertains to only one cross-section of the transistor.

S. G. Ellis

S. G. Ellis

Appendix I

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:

10 cc HF
10 cc H_2O_2
40 cc H_2O

No. 3:

56 cc HF
56 cc HNO_3
12.5 cc H_2O

No. 4:

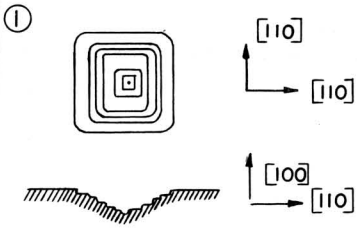
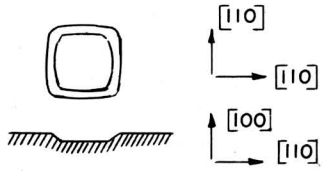
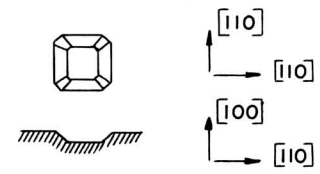
50 cc HNO_3
30 cc CH_3COOH
30 cc HF
0.6 cc Br

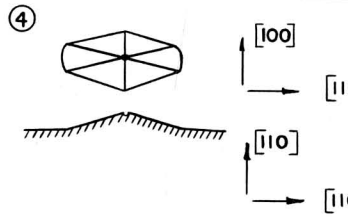
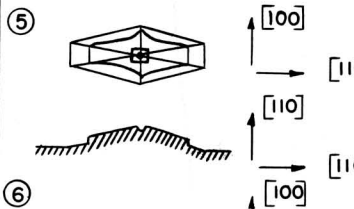
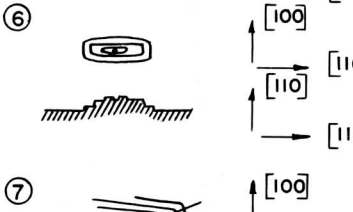
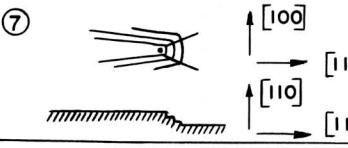
Silver Etch:

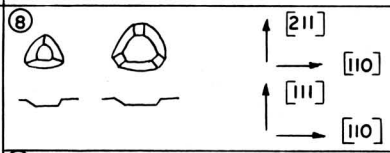
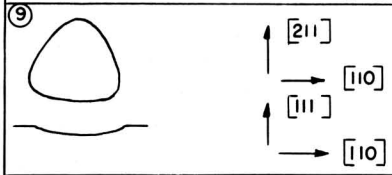
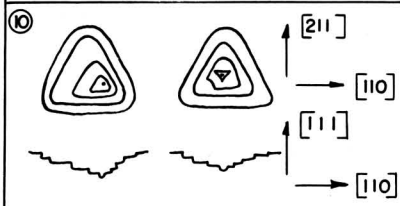
40 cc HF
20 cc HNO_3
40 cc H_2O
2 gm $AgNO_3$

Appendix II

THE PIT SHAPES ARE SHOWN FIRST AS THEY WOULD APPEAR UNDER VERTICAL ILLUMINATION. BENEATH THIS IS SHOWN A VERTICAL CENTER SECTION OF THE STRUCTURE. THESE PITS ARE BEST VIEWED AT X100 OR HIGHER MAGNIFICATION.

SURFACE	ETCH	PIT SHAPE AND ORIENTATION	INTERPRETATION AND NOTES
(100)	I	① 	THE CHARACTERISTIC FEATURE IS THE CENTER DOT WHICH APPEARS BRIGHT ON RACKING UP FROM FOCUS. THIS PIT FORMS AT THE INTERSECTION OF AN EDGE DISLOCATION WITH THE SURFACE. THE TERRACES PROBABLY INDICATE JOGS IN THE DISLOCATION. SIZE OF PITS VARIABLE UP TO ABOUT 20μ ALONG AN EDGE. THESE CAN AGGREGATE TO FORM SMALL ANGLE GRAIN BOUNDARIES.
		② 	THE CHARACTERISTIC FEATURE IS THE ABSENCE OF A CENTER DOT. THE CAUSE OF SUCH PITS IS UNKNOWN. GROUND SURFACES ETCH WITH THIS PIT FORM. THE SIZE IS VERY VARIABLE RANGING UP TO 20–40μ FOR FORM ②. FORM ③ IS GENERALLY SMALLER.
		③ 	

SURFACE	ETCH	PIT SHAPE AND ORIENTATION	INTERPRETATION AND NOTES
(110)	II	④ 	THE CHARACTERISTIC FEATURE IS THAT THE CENTER ETCHES HIGHER THAN THE SURROUNDING SURFACE. BOTH ④ AND THE TERRACED FORM ⑤ ARE PROBABLY THE SITE AT WHICH AN EDGE DISLOCATION MEETS THE SURFACE. THE SIZES RUN UP TO 10x20μ FOR FORMS ④ AND ⑤. ⑥ IS SMALLER AND IS PERHAPS THE BEGINNING FORM OF A STRUCTURE SUCH AS ⑤ ⑦ IS A TERRACED FORM SEEN WHEN THE ORIENTATION OF THE SURFACE ETCHED IS NOT ACCURATELY (110). THE DOT IS RAISED WITH RESPECT TO THE GENERAL SURFACE.
		⑤ 	
		⑥ 	
		⑦ 	

SURFACE	ETCH	PIT SHAPE AND ORIENTATION	INTERPRETATION AND NOTES
(111)	II	⑧ 	THERE IS NO CENTER SPOT IN THESE PITS. SIZES UP TO 15μ—VERY VARIABLE.
		⑨ 	PROBABLY A TERMINAL FORM OF ⑧ USUALLY LARGE — UP TO 40μ ON A SIDE.
		⑩ 	THESE TERRACED FORMS PROBABLY INDICATE EDGE DISLOCATIONS, THE TERRACES BEING DUE TO JOGS IN THE DISLOCATIONS. THE CHARACTERISTIC FEATURE IS THE CENTER DOT - WHICH NEED NOT HOWEVER BE CONCENTRIC WITH THE OUTER TERRACES . PARTS, OR THE WHOLE OF A TERRACE MAY BE ROTATED 60° WITH RESPECT TO THE USUAL ORIENTATION.