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LB-926

RECRYSTALLIZATION OF GERMANIUM FROM INDIUM SOLUTION

RADIO CORPORATION OF AMERICA

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Recrystallization of Germanium from Indium Solution

Approved

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Introduction

This bulletin discusses work done on the recrystallization of germanium from its solution in indium. The purpose of the experiment was to obtain a large-scale recrystallized region in the germanium-indium system so that a better insight in the process of making alloy-junction devices would result. In particular, it was sought to examine whether the progress of the alloying front, i.e., the liquid-solid interface, is affected by crystallographic orientation, whether a uniform junction can be obtained and how perfect a recrystallized region can be produced.

The penetration of the alloy front into germanium determines the geometry of the region between the two junctions of a transistor. Both the current-amplification factor and the transit-time dispersion of minority carriers are affected by this geometry.

Uniformity of the junction is desirable in order to obtain a high and sharp breakdown voltage. The breakdown voltage of a junction is shown by the V-I characteristic which presents the sum of the current contribution from every region of the junction. Hence a "soft" breakdown voltage may be attributed to a non-uniform junction.

The homogeneous recrystallized p-type region forms a single crystal with the underlying n-type germanium as in the grown junction. However, the transition between the n and p regions is very abrupt in contrast to the more gradual transition of the usual grown junction. Also, the recrystallized region is of very low resistivity. This is desirable for the emitter of a p-n-p transistor.

The Experiment

A single crystal of germanium originally grown in the 111 direction was cut into a cylinder with its axis in nearly the 110 direction. This particular orientation was selected because a cross section of the cylinder normal to this direction exposes the three major axes (see Fig. 1).

After etching, the crystal was dipped into a pot of indium which was brought to 600 degrees C in an inert atmosphere in a manually regulated Globar furnace. The crystal was clamped by a carbon ring supported by the pot as shown in Fig. 2, so that the immersed surface was spaced from the surrounding walls. The phase diagram for the indium-germanium system[1] shows that at 600 degrees C the equi-

[1] W. Klem, et al, "The Behavior of the Elements of Group III With One Another and With the Elements of Group IV, *Z. Anorg. Chem.*, Vol. 256, p. 239 (1948). Also LB-890, *Purification of Germanium by Gradient Freezing*.

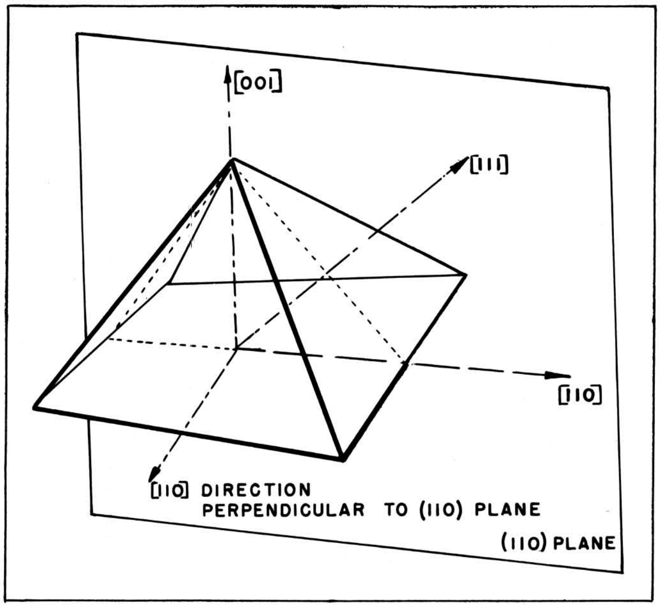

Fig. 1 - Half of octahedral unit cell showing how 110 plane contains the three major axes.

librium concentration of germanium dissolved in indium is 20 atomic per cent. The temperature was reduced from 600 degrees C to 100 degrees C in about two hours. Initially, the temperature

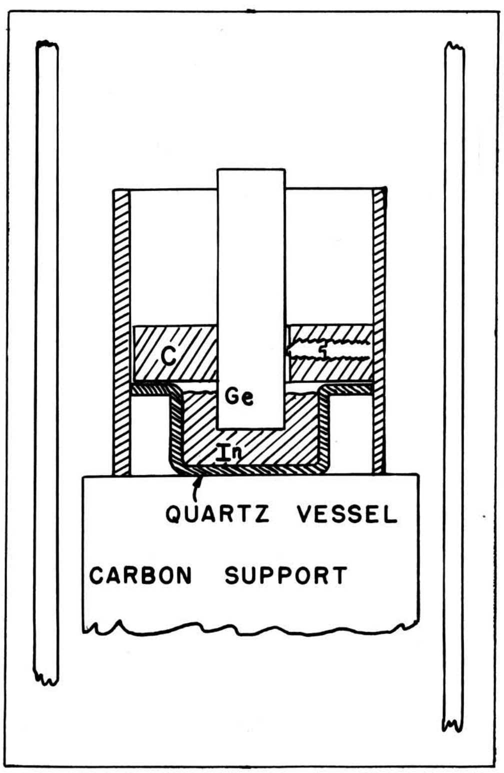

Fig. 2 - Setup in the Globar furnace. The germanium crystal descends into the indium as soon as the indium melts, and assumes the position shown.

was lowered at an even slower rate than the above average of 250 degrees C per hour.

The indium was dissolved away by immersion in mercury followed by a short nitric acid etch which removed the last visible traces of indium and mercury without attacking the germanium.

The External Observations

The cleaned crystal exhibited the spectacular array of needles shown in Figs. 3, 4 and 5.

As the temperature was lowered, germanium atoms from the supersaturated solution grew back onto the original crystal in epitaxial fashion. The greatest crystal growth was in the 100 direction, forming needles which grew up to the walls of the container, and leaving voids between the needles and holes within their structure. These 100 needles are made up of sets of four octahedron facets stacked up like hollow pyramids. These are 111 facets with triangular boundaries about 1 mm on the side. Many of these facets are incomplete, i.e., only their edges have formed. These are 110 edges which usually make 111 facets grow faster along their plane than in thickness.

A few twins have been found (horizontal facet at upper left of Fig. 3 and triangles at left and right of Fig. 5).

Fig. 5 is a view along the 100 axis. Since most terminal 111 facets are incomplete one can see only the 110 edges meeting at the apex of the needles and forming a pattern of crosses, except for occasional twins which show up as triangles. Although recrystallization proceeded up to the walls of the container, the non-cylindrical appearance of the specimen is due to the fact that some of the needles broke off.

The Internal Observations

The specimen was cut in the plane of the three major axes, the 110 plane. After lapping, the exposed surface was etched to reveal the p-n junction. This is shown in the composite

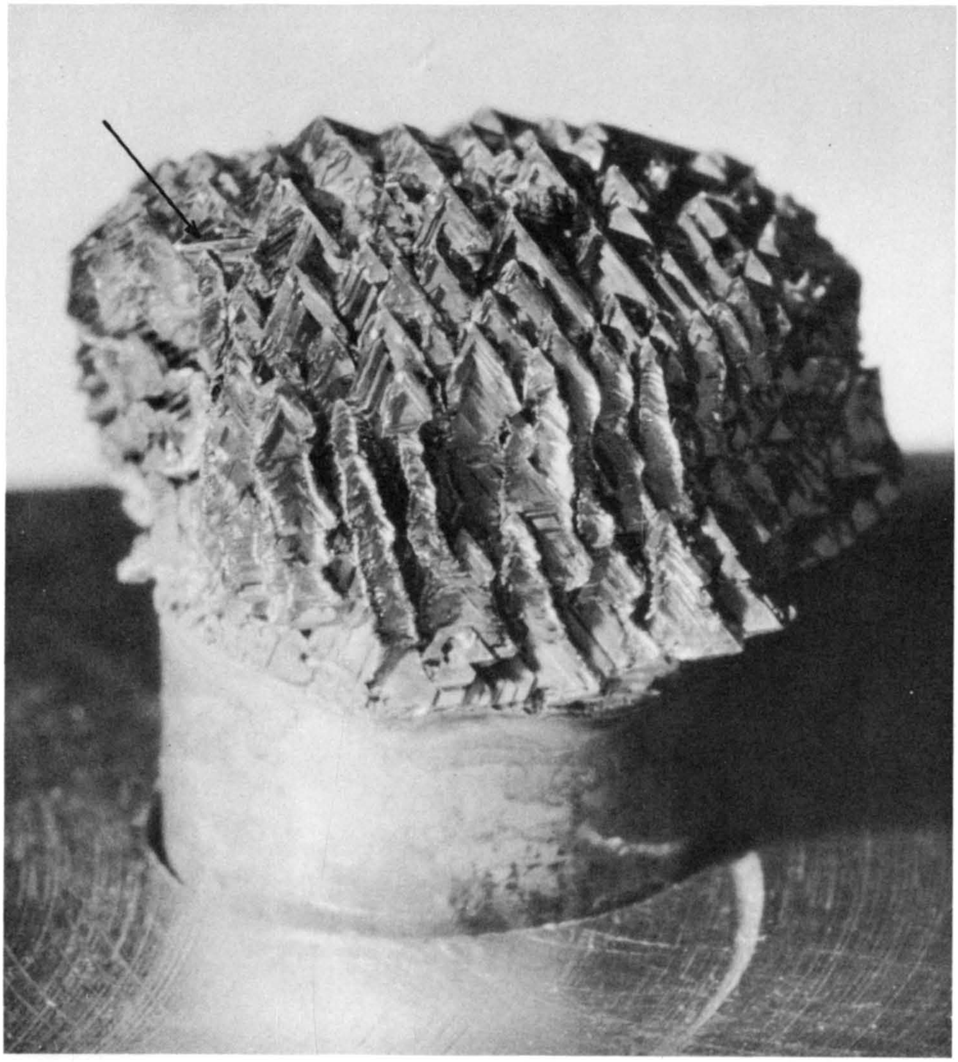

Fig. 3 – A view of the recrystallized germanium. The arrow points to the twin. Note the stacked-up needle formation.

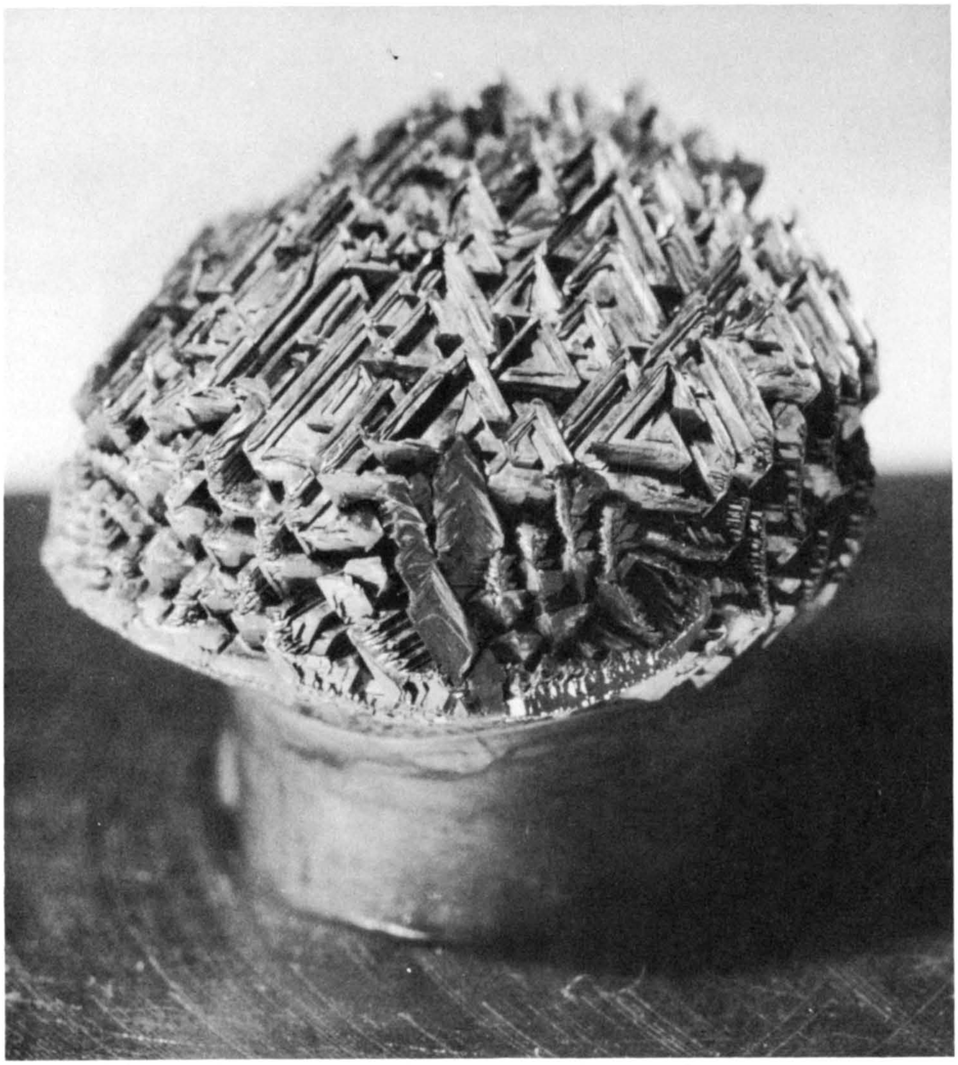

Fig. 4 – Another view of the recrystallized germanium showing the hollow 111 facets.

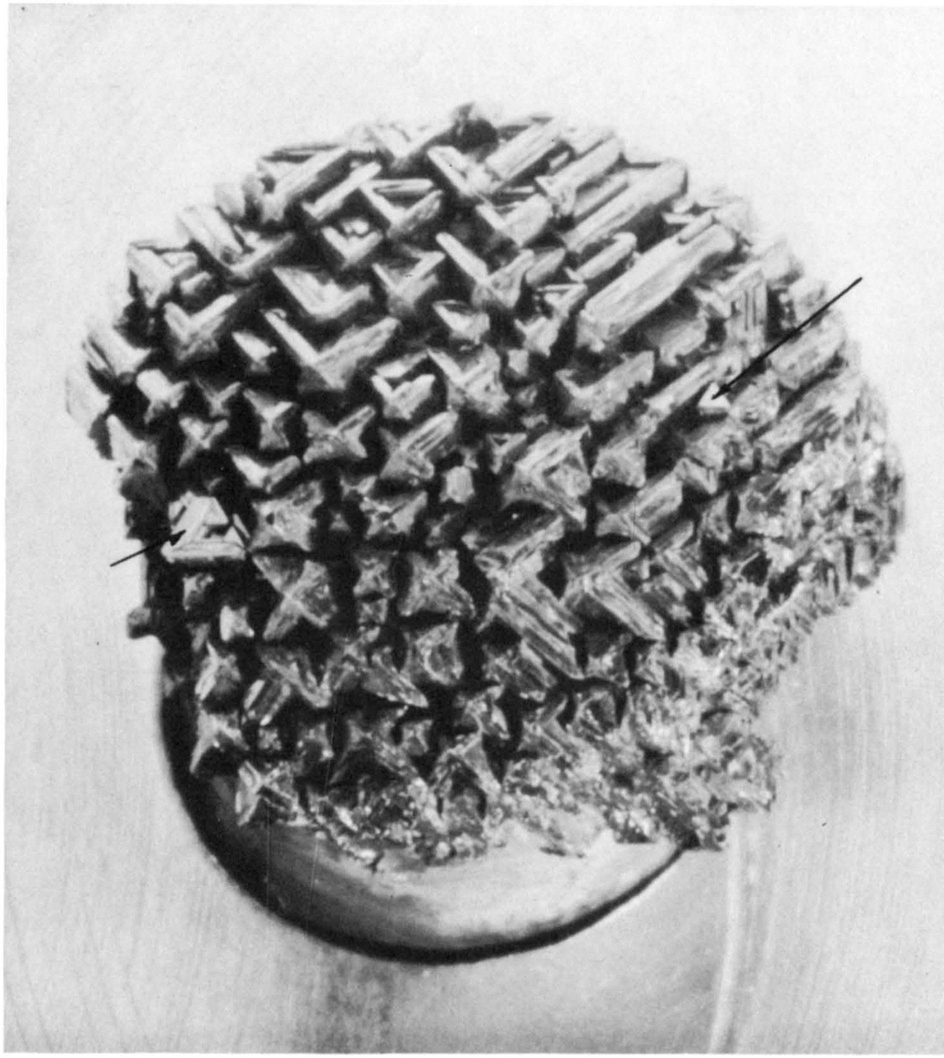

Fig. 5 - A third view of the recrystallized germanium looking down the 100 axis. The arrows point to the twins.

photograph of Fig. 6 as a white line at the base of the recrystallized region. From etching studies there is evidence that the region outside the p-n junction consists of recrystallized germanium. Hence it may be concluded that the junction runs very close to what was the liquid-solid interface at 600 degrees C. Initially, the recrystallization forms an overgrowth or continuous layer which includes numerous large pits. X-ray diffractions confirmed that the overgrowth region is a crystallographic continuation of the underlying seed crystal. The overgrowth region appears to be thinnest in the 100 direction but can be as thick as 100 microns in other directions. In this 110 plane no correlation could be made between penetration of the alloy front and crystallographic orientation. The interpretation is hindered by the fact that the initial

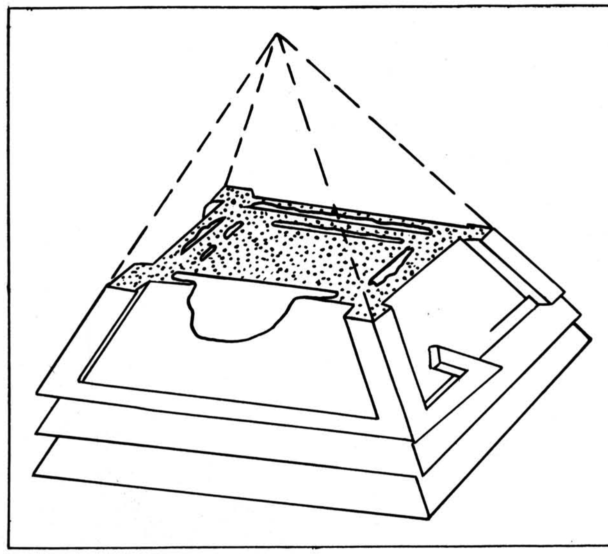

Fig. 7 - Illustrating the internal appearance of a 100 needle.

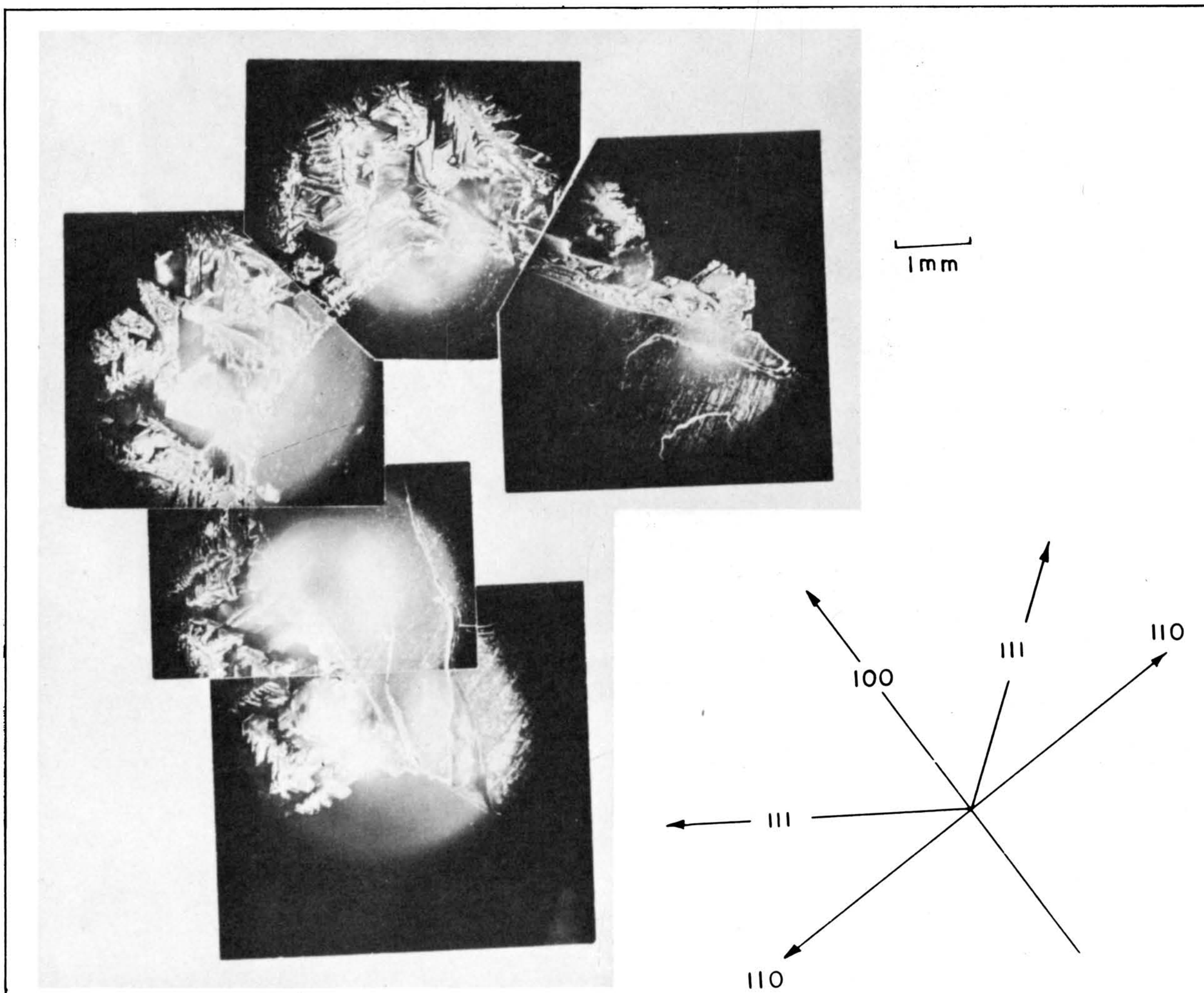

Fig. 6 - Cross section of the specimen in a 100 plane. The p-n junction is the fine line, mostly white, at the base of the recrystallized region.

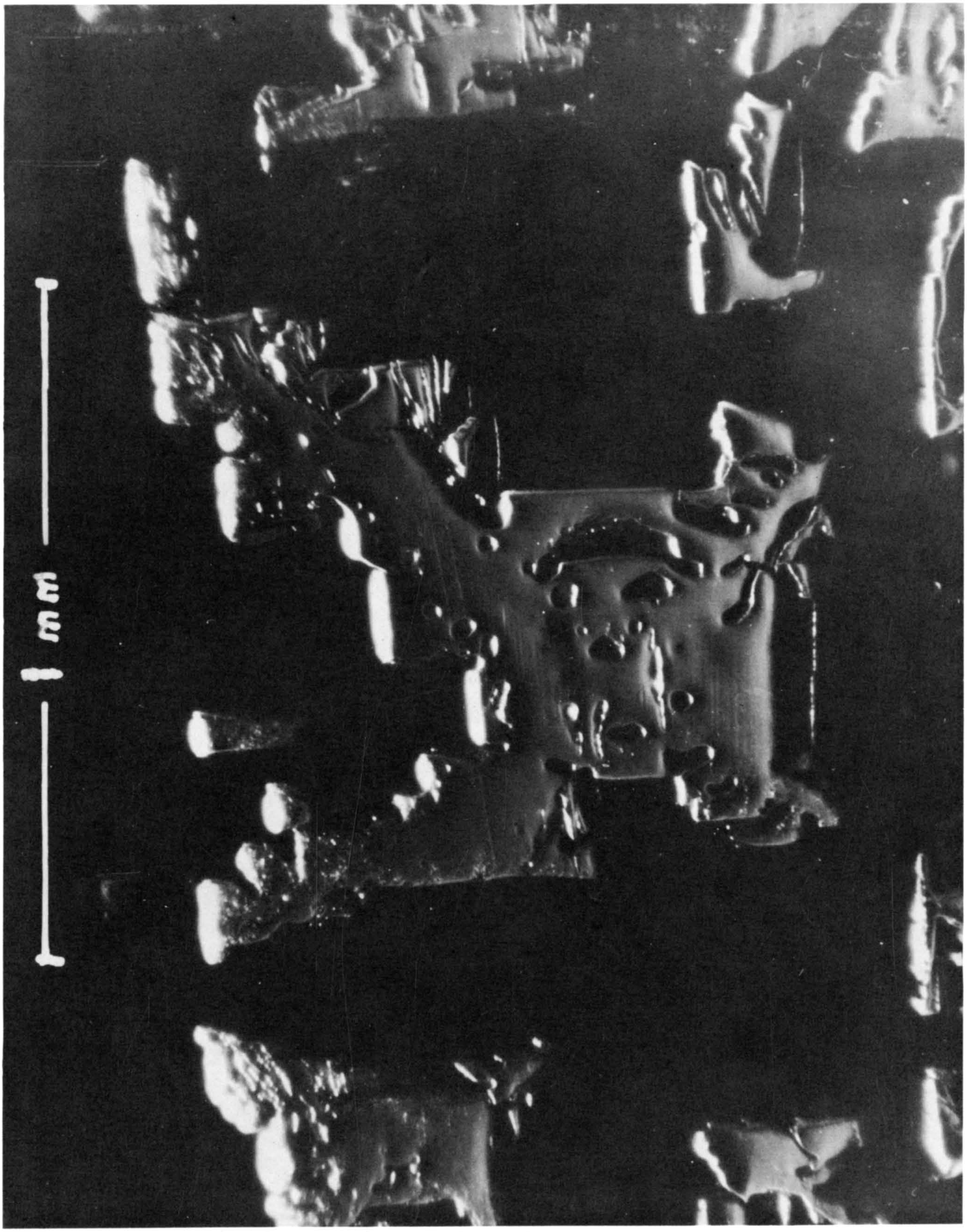

Fig. 8 - Cross section of a 100 needle in a 100 plane. Note the increased pitting due to the acid etch at the extremities remote from the center of the needle.

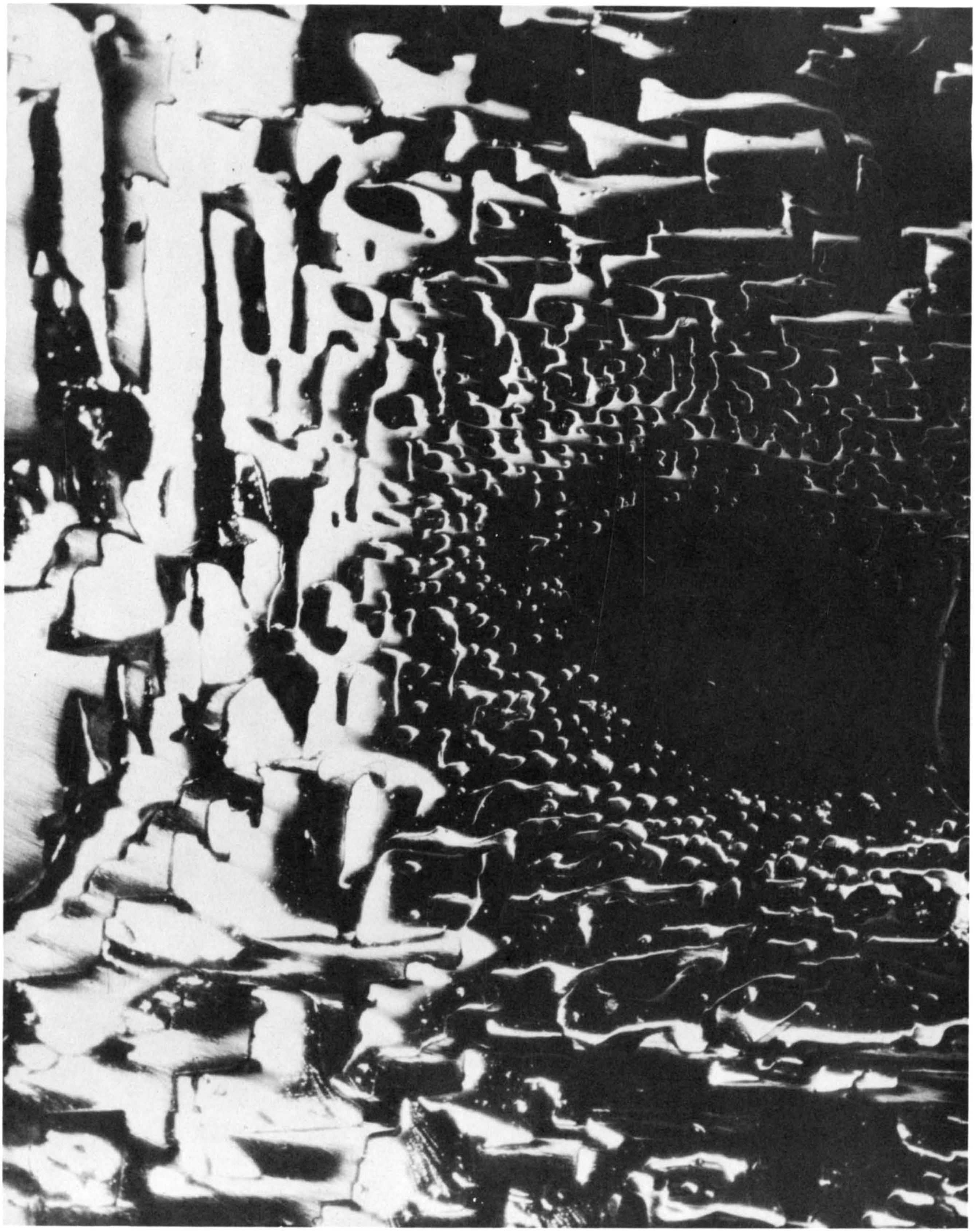

Fig. 9 – Cross section of most of the crystal in the 100 plane. The dark oval shaped region is the parent crystal. The pitted region is the recrystallized germanium.

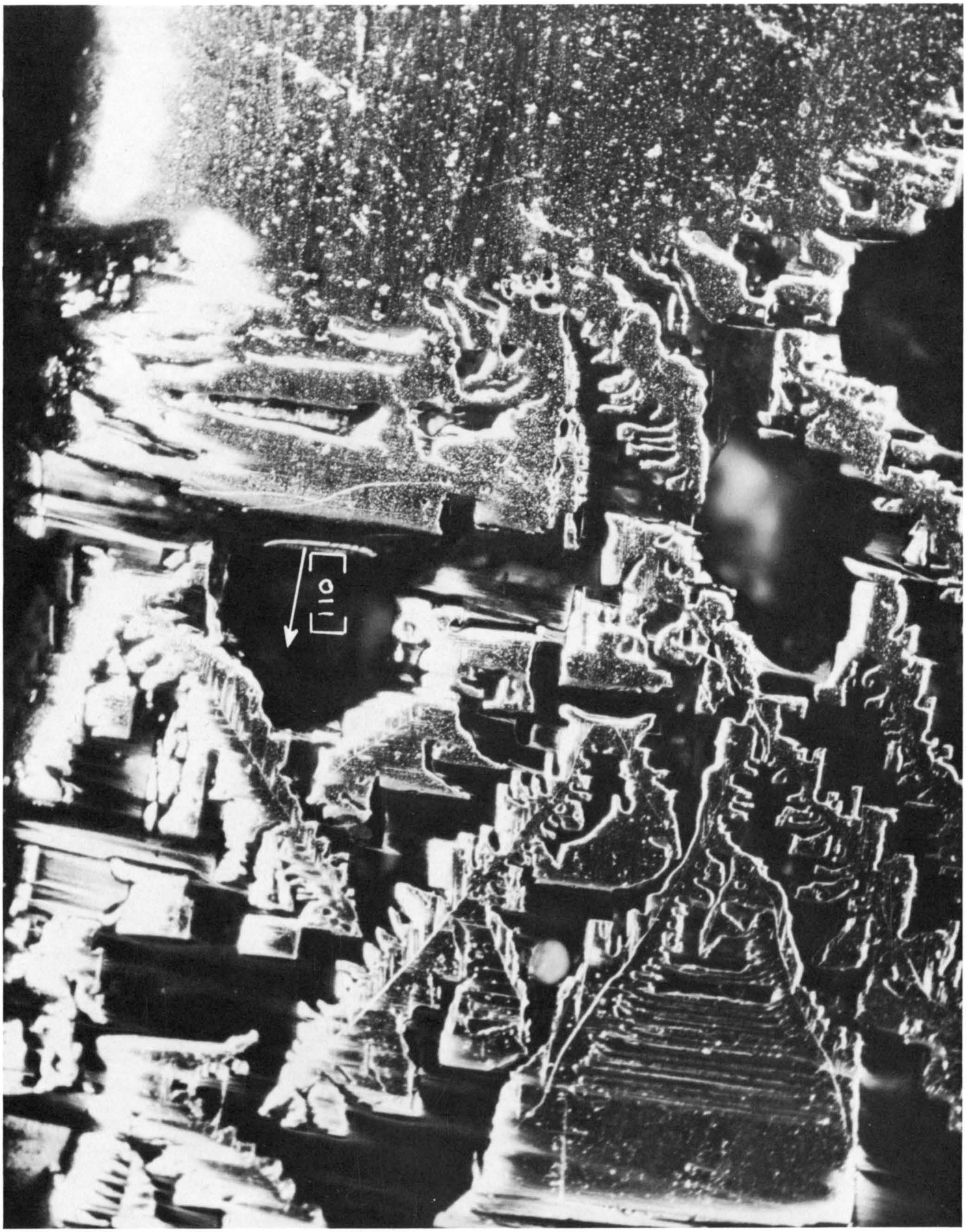

Fig. 10 – Cross section of a recrystallized region in the 100 plane. The parent crystal is at the top. Note the thick overgrowth region in the 110 direction (arrow), and at the lower right hand corner the stack of 111 facets appearing in cross section.

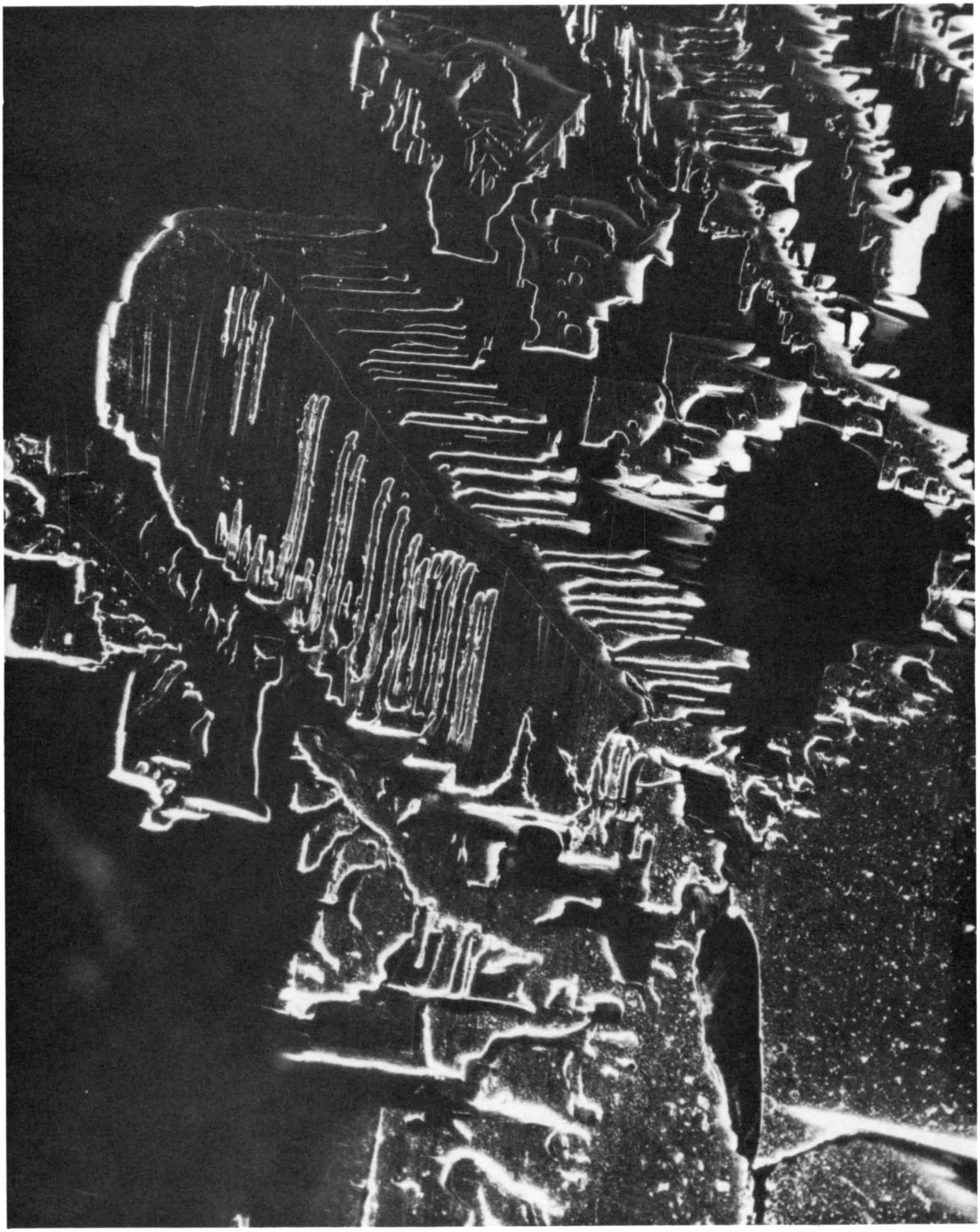

Fig. 11 – Cross section of another recrystallized region in the 100 plane showing cross section through a 100 needle. Note the long etch line, the line structure at 45 degrees to it, and the stack of 111 plates.

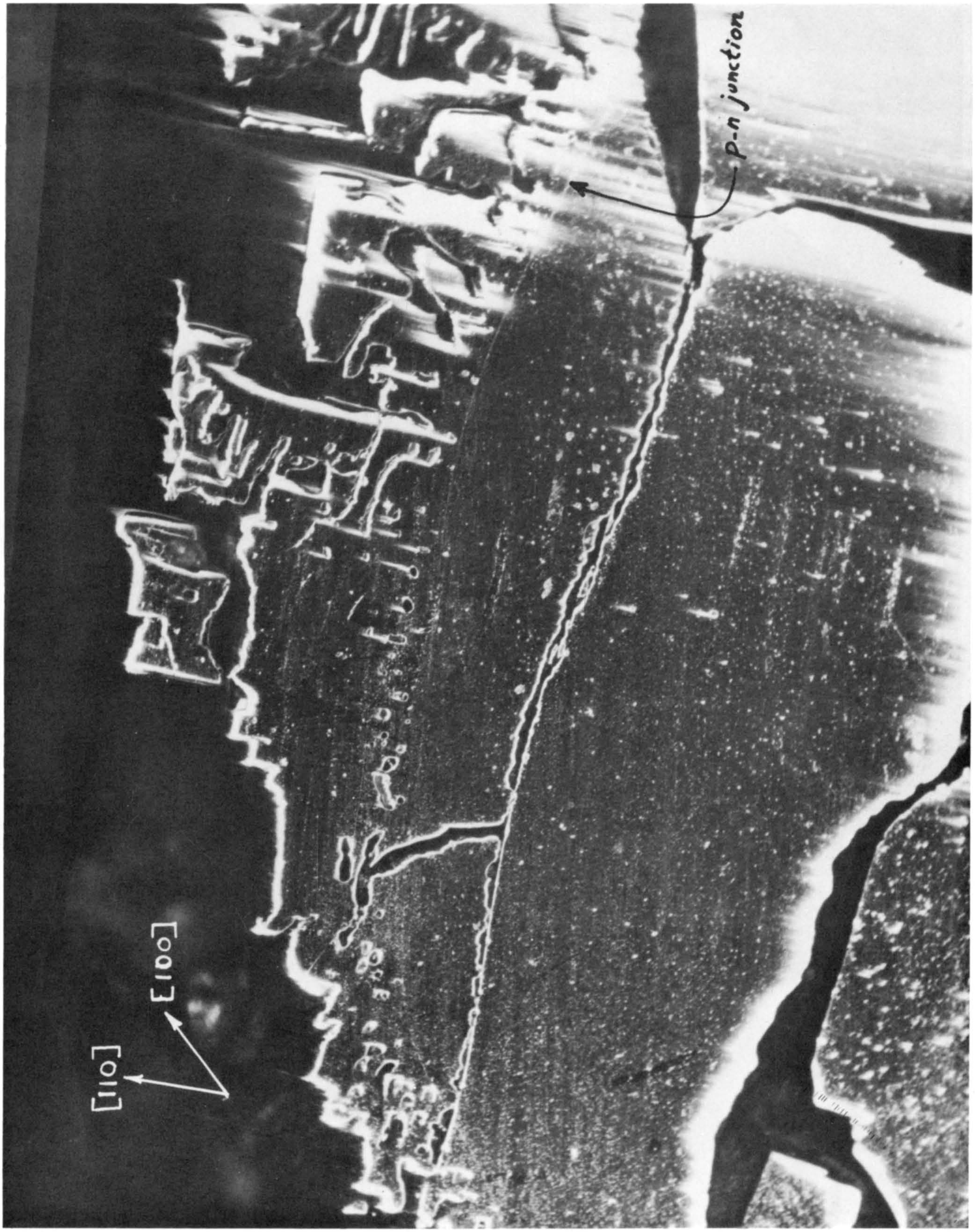

Fig. 12 - Cross section of still another recrystallized region in the 100 plane. The arrow points to the p-n junction. Note that the overgrowth layer is thicker in the 110 direction than in the 100 direction.

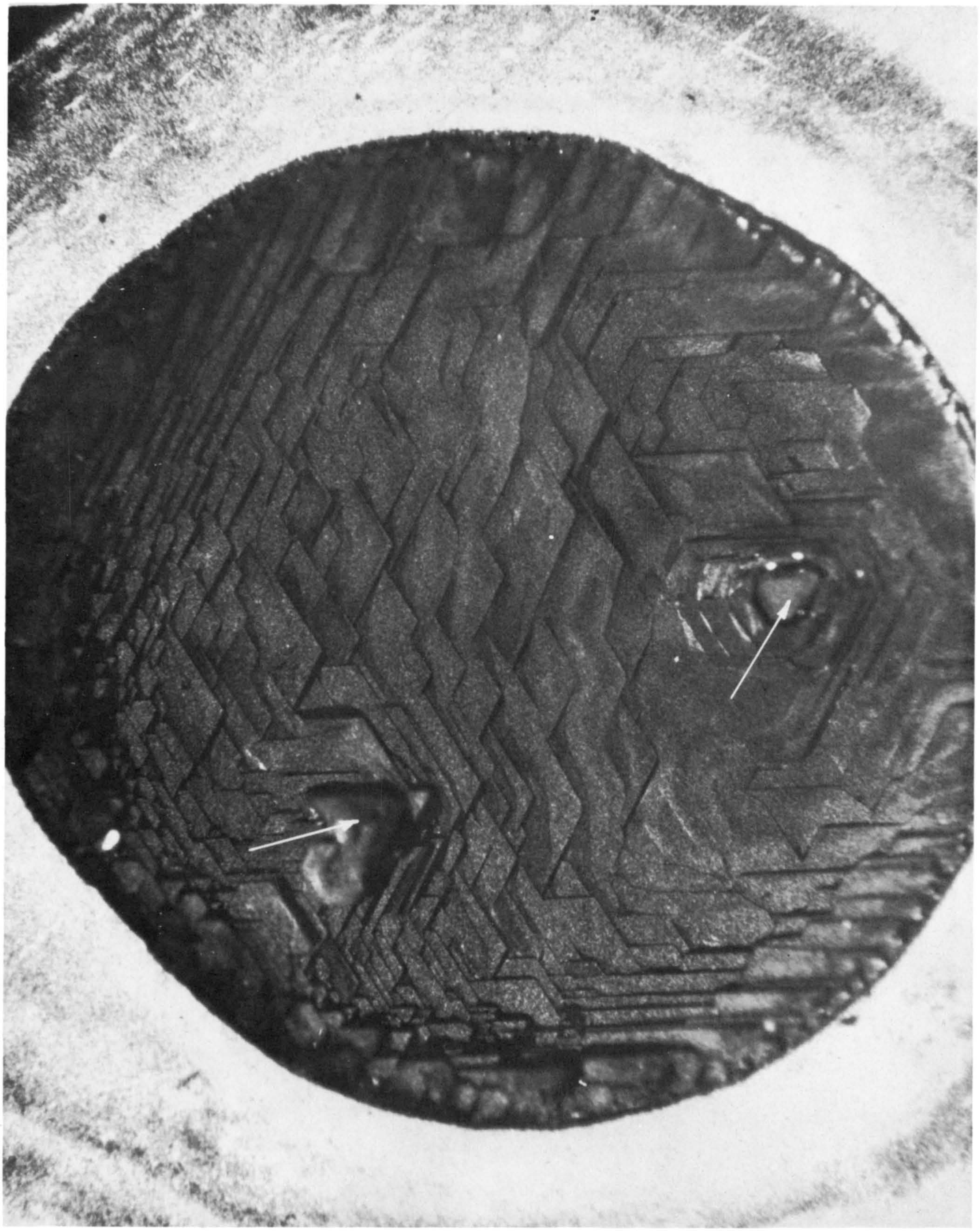

Fig. 13 - Photograph of the recrystallized region at the collector of a p-n-p transistor. The zig-zagging pattern is formed by the exposed edges of overlapping 111 plates. The arrows point to poorly wetted regions.

boundary condition consisted of flat plane intersecting a cylinder. A better resolution would have been obtained had a spherical surface been chosen instead of a cylinder.

A cut in the 100 plane, across one of the needles is shown in Figs. 7 and 8. These show how 111 facets are separated by empty spaces, the outer side of the 111 plate being more perfect than the inner side. As the solution is cooled, the concentration of germanium in solution increases radially away from the center of the crystalline needle so that the needle tends to grow towards those regions of the solution which are richest in germanium. As crystallization proceeds, more indium atoms get trapped in the newly formed layers. As shown in Fig. 8, the extremities of the recrystallized region exhibit more pits due to acid etching than the center. This suggests a faster etching rate, in agreement with the greater defect concentration in the last material to crystallize. It has been observed at RCA Laboratories that there is a limit to the number of indium atoms which can be included in the germanium lattice, and that for maximum indium concentration the specific resistivity of the material is about 0.001 ohm-cm, the material remaining a semiconductor. Hence one should expect that in the present experiment the recrystallized germanium is still a semiconductor and has a resistivity of about 0.001 ohm-cm.

Fig. 9 shows a cross-section of the whole crystalline system in the 100 plane after a light etch which was sufficient to reveal the junction. The original crystal is the lightly pitted oval shaped region. The size and number of pits increases radially. The p-n junction, not visible on the photograph, runs along the inside of the inner ring of coarse pits.

Figs. 10 and 11 show long etch lines which wave about the 100 axis. At 45 degrees to the 100 axis a fine structure of line spreads on either side of the central etch line and coincides with 111 planes.

Fig. 12 is a cross-section in the 100 plane. It shows that the recrystallization is more homogeneous and thicker in the 110 direction than in the 100 direction. This photograph also shows that the p-n junction is nearly a straight line in the 110 plane.

The Practical Case

In making alloy-type junctions a pellet of indium is fused to the flat surface of a germanium wafer. The liquid-solid interface assumes a concave configuration. Now, recrystallization can take place from the seed surface inward (instead of outward as in the case described above). Germanium from the supersaturated solution condenses into well-ordered overlapping plates lying in 111 planes (see Fig. 13). Regions which have not been wetted properly remain at the original level of the crystal surface or protrude from the concave bottom and are seeds for bulkier recrystallization, i.e., the recrystallized material in these regions forms an assemblage of octahedrons instead of 111 plates. When the indium wets uniformly a germanium surface which has been exposed as a 111 plane, the recrystallized 111 plates tend to grow together to form a homogeneous recrystallized region.

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