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METHOD OF PLASTIC WORKING OF SEMICONDUCTORS

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Fig. 1.

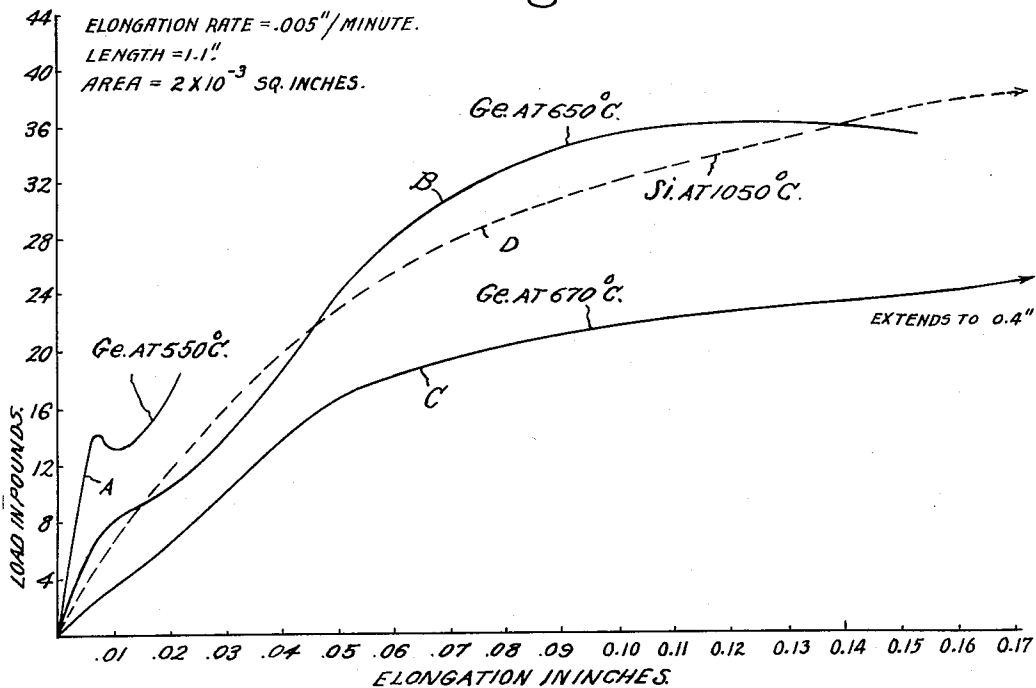
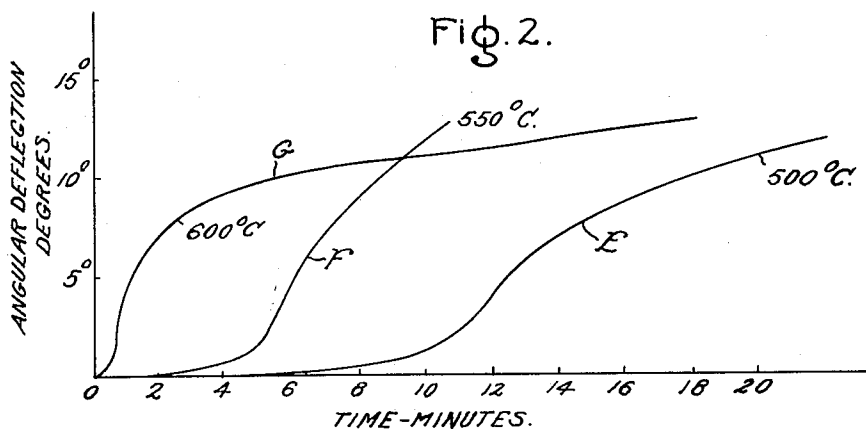


Fig. 2.



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METHOD OF PLASTIC WORKING OF SEMICONDUCTORS

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2 Claims. (Cl. 148—11.5)

My invention relates to methods of working or fabricating monatomic semiconductor members and more particularly to methods of plastic forming of a semiconductor element into members having various configurations normally unattainable or very difficult of attainment with conventional methods of working semiconductors.

Monatomic semiconductors, such as germanium or silicon, are normally employed as the conduction control member in various photoelectric, thermoelectric and asymmetrically conductive devices. These semiconductor members are usually simple rectangular or disk-shaped wafers formed by diamond saw cutting from a solidified ingot often together with a subsequent abrasive grinding of the wafer thus extracted. In order to obtain single crystalline material, the solidified ingot is often produced by seed crystal growth from a melt of the semiconductor material. Because of the extreme hardness, brittleness, and strong cohesive quality of its stable and symmetrical diamond-type cubic lattice structure, all attempts to form or plastically work these semiconductors in their solid state have heretofore resulted only in fracturing the semiconductor body. Consequently, semiconductor members having unusual curved, bent, or filamentary shapes were either unattainable or could only be attained by relatively cumbersome, expensive, and wasteful methods such as by diamond saw cutting and grinding the semiconductor in a solid state or by molding the semiconductor while in a liquid state.

Accordingly, an important object of my invention is to provide a method for plastically working monatomic semiconductors such as germanium and silicon.

Another object is to provide semiconductor members having unusual curved or deformed configurations.

Another object of my invention is to provide a method for controlling the electrical characteristics of plastically deformed semiconductors.

The invention, together with further objects and advantages thereof, may be easily understood by referring to the following description taken in connection with the accompanying drawing in which Fig. 1 contains typical stress-strain curves obtained in practicing the invention; and Fig. 2 contains curves illustrating the time delay involved in deforming semiconductors at certain temperatures.

In accord with my invention, although germanium and silicon semiconductors are not amenable to plastic working at room temperatures; I have discovered, contrary to common belief, that they may be effectively and easily worked plastically under suitable pressure and time while being maintained at elevated temperatures between 65% and 85% of the absolute temperature melting point of the semiconductor involved. After being deformed at the elevated temperature, the semiconductor member is allowed to cool to room temperature and retains its deformed shape although it reacquires its initial hard and brittle character. As the temperature of the semiconductor is raised above the minimum "yield temperature" corresponding to approximately 65% of the absolute melting point, the deforming stress and time required to produce a given deformation decreases rapidly such that

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at temperatures above 70% of the absolute melting point, the material becomes highly malleable and ductile, such that it may be easily pressed, elongated, bent, or otherwise deformed. Below this 65% minimum yield temperature, the elastic limit (yield point) of the semiconductor is substantially equal to its ultimate strength, such that the material tends to fracture rather than deform if stressed beyond this elastic limit.

More specifically, germanium becomes gradually deformable to a limited extent at approximately 500° C. (773° K.), corresponding roughly to 65% of its absolute temperature melting point (1214° K.) if subjected to a deforming force between 100 and 3,000 pounds per square inch for several minutes; and that at temperatures above 627° C. (900° K.), the germanium becomes immediately and greatly deformable with a deforming force between 50 and 15,000 pounds per square inch. This means that at temperatures above 627° C. there is a very wide range of stress which can be applied to produce plastic deformation without fracture. Below 600° C. (873° K.) it is preferable, in order to avoid fracture, that the deforming force be less than 8,000 pounds per square inch, and that the germanium be allowed to deform gradually over a short interval of time such as a few minutes. The extent of permissible deformation increases as the temperature increases. At temperatures above 760° C. (1034° K.), corresponding to approximately 85% of its absolute temperature melting point, the germanium becomes exceedingly malleable and ductile; but problems of oxidation and the tendency of the germanium to alloy with or accept impurities from the working tool make temperature above 760° C. rather unsuitable for plastically working germanium. The best conditions for most plastic working operations on germanium are over a temperature range of from 600° C. to 700° C., and with forces ranging from 100 to 10,000 pounds per square inch depending upon the temperature employed and the degree of deformation desired.

Similarly, silicon becomes initially gradually deformable at a minimum yield temperature of approximately 830° C. (1103° K.), corresponding roughly to 65% of the melting point (1693° K.) of silicon on the absolute temperature scale. Silicon likewise becomes increasingly deformable at temperatures above this minimum yield temperature until at 1165° C. (1438° K.), corresponding to 85% of its absolute temperature melting point, it is readily deformable under stresses less than 500 pounds per square inch. In general, silicon behaves the same as germanium at temperatures corresponding roughly to the same percentage of their melting points on the absolute scale, with the exception that silicon requires stresses approximately 1.5 to 2 times greater than germanium in order to obtain equivalent deformation. The best working conditions for most plastic working operations on silicon are over a temperature range of from 900° C. to 1100° C. and with forces ranging from 500 to 25,000 pounds per square inch, depending upon the temperature employed and the degree of deformation desired.

This plastic deformation of semiconductors tends to increase the resistivity of the semiconductor. For many applications of semiconductors, it is desirable to employ a semiconductor member having a predetermined resistivity characteristic. In accord with a further feature of my invention, I have found that the initial bulk resistivity characteristic in germanium as well as the uniformity of electrical characteristics can be substantially restored or controlled to a predetermined desired value by annealing the deformed germanium, either before or after the deformed germanium is allowed to cool, at a temperature in the neighborhood of 500° for an extended period of time, at least 12 hours, and preferably about 24 hours. For example, the resistivity of a germanium member hav-

ing an initial bulk resistivity of 2 ohm centimeters increased to 4 ohm centimeters upon being deformed and returned substantially to 2 ohm centimeters after being annealed for 24 hours at 500° C.

In order that those skilled in the art may better understand how the present invention may be carried into effect, certain exemplary tests are described below and illustrated in the accompanying drawings.

In one series of tests, small bars of germanium having a purity corresponding to a resistivity in the range of 2 to 20 ohm centimeters were supported by end clamps in a vertical position within an air oven. The bars were heated within the oven to temperatures between 500° C. and 700° C. One end of each heated bar was maintained immobile while the other end was pulled at a constant elongation rate by an instrument which continually measured the instantaneous stress. Slip lines were observed in all such tensilely stressed germanium specimens, and these slip lines appear to be along (1-1-1) planes of the germanium. The germanium retained its elongated shape upon cooling to room temperatures. Typical resulting stress-strain curves at three temperatures, 550° C., 650° C., and 670° C. for single crystal germanium bars 1.1 inches long having a square cross-section of approximately 2×10^{-3} square inches and drawn at an elongation rate of .005 inch per minute, are shown in Fig. 1 as curves A, B, and C respectively.

Curve A shows that at 550° C. there is a short initial elastic region and a small plastic region between the elastic limit and the breaking point. At 650° C., as indicated by curve B, there is a very small elastic region and a considerable plastic region before breaking under a stress corresponding to about 18,000 pounds per square inch. At 670° C. and above, as indicated by curve C, there is substantially no elastic region, the germanium becoming permanently deformable under very low stresses and allowing an elongation as high as 35% before breaking under a load of the order of 15,000 pounds per square inch. At temperatures below 600° C., the elongation rate should be less than 1% per minute in order to avoid fracture. At temperatures in the neighborhood of 700° C., the elongation rate may be somewhat faster but should not exceed 5% per minute.

Similar tests with silicon bars show similar elongations at temperatures corresponding to the same percentage of its absolute temperature melting point, but require greater stresses. A typical stress-strain curve for a 1 inch silicon bar having a cross-sectional area of 2×10^{-3} square inches at 1050° C. is shown as curve D in Fig. 1.

In another series of tests, small bars of highly purified germanium were supported by a clamp at one end in a horizontal position within an oven. The bars were heated to temperatures between 500° C. and 700° C. and subjected to a vertical stress by suspending a known weight from their opposite unsupported or "free" ends. At temperatures above 650° C., the bars bend immediately around the support point without fracture with low stresses less than 1,000 pounds per square inch. At temperatures below 600° C. and with low stresses of the order of 1,000 pounds per square inch, there is a noticeable time delay between the application of the stress and the resulting angular bending. This latter phenomenon is illustrated by the curves E, F, and G of Fig. 2 wherein the amount of angular deflection of three similar single-crystal germanium bars is plotted against time for three temperatures, 500° C., 550° C., and 600° C., respectively. The bars tested and represented by these curves were single crystal bars of N-type germanium of approximately 1 millimeter square cross-section with a purity corresponding to a resistance range of 2 to 20 ohm centimeters. A 100 gram weight was suspended from each bar at a point 1 centimeter away from the clamping point. As can be seen from the curves of Fig. 2, at 500° C. more than ten minutes was required before any appreciable deformation

took place; at 550° C., the bar involved began to deform noticeably after five minutes; while at 600° C., the bar involved deformed after less than one minute. Larger stresses decreased the bending time. Above 600° C., similar germanium bars deform substantially immediately after the application of a similar stress. Slip lines are also observed in all of the bent specimens which are apparently also along the (1-1-1) planes of the deformed material. These slip lines disappear if the specimen is etched. With larger specimens, the bending is accompanied by audible clicks.

Similar bending tests with horizontal silicon bars supported at both ends and subjected to a central vertical stress showed behavior similar to that of germanium at temperatures corresponding to the same percentage of their melting points, with stresses from 1.5 to 2 times as great as those required for germanium under similar testing conditions. At 900° C., for example, a 2.5 pound weight applied at the center of a 1 millimeter square cross-section silicon bar supported at points spaced 0.5 inch apart produces a gradual small angular deformation over a period of a few minutes, while at 1,000 C., the same weight produces an immediate and greater angular deformation.

In another series of tests, rectangular wafers of high purity germanium of about $\frac{1}{2}$ to $\frac{3}{4}$ inches in length and width and about $\frac{1}{4}$ " in thickness were heated to 700° C. and placed within a hydraulic press between two steel blocks which had also been preheated to 700° C. A 50% reduction in thickness of these wafers was easily produced at this temperature with a pressure less than 100 pounds per square inch.

It will thus be seen that semiconductors, such as germanium and silicon, can be made malleable, ductile, and bendable by raising its temperature to a temperature at least 65% of its absolute temperature melting point and preferably within a temperature range of between 70% and 80% of its absolute melting point. The semiconductors may be bent, elongated, or squeezed into various shapes with comparatively low metal-working stresses while the material is maintained at such elevated temperatures and then allowed to cool, whereupon it retains its deformed shape. Moreover, if germanium of predetermined resistivity is required, the initial resistivity characteristics can be substantially restored by annealing the deformed germanium body at approximately 500° C. for an extended period of time, preferably before the semiconductor member is allowed to cool to room temperature.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of plastically working crystalline germanium, which method comprises heating the germanium to a temperature between 500° and 760° centigrade, applying a deforming force to the germanium while it is maintained at this elevated temperature, and annealing the deformed germanium at approximately 500° centigrade for an extended period of time.

2. The method of plastically working single crystal germanium, which method comprises heating the germanium to a temperature between 500° and 760° centigrade, applying a deforming force to the germanium while it is maintained at this elevated temperature, annealing the deformed germanium at approximately 500° centigrade for at least 12 hours, and allowing the annealed germanium to cool to room temperature.

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