Sept. 18, 1956 C. H. POOL 2,763,608

ELECTRO-CHEMICAL TREATMENT

Filed June 23, 1953

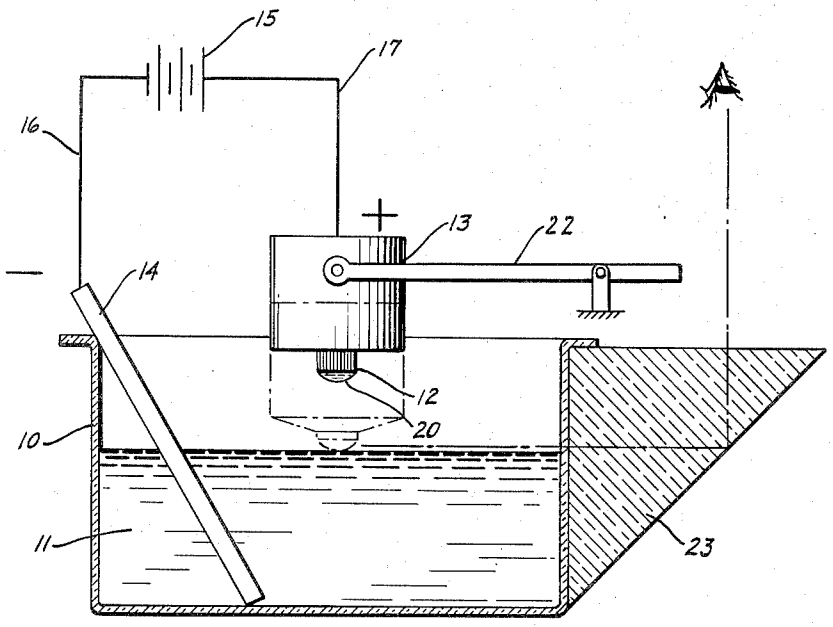


FIG. 1.

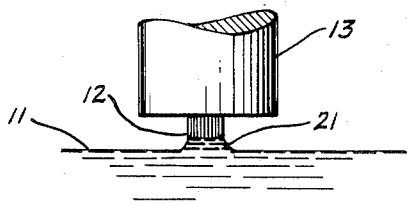


FIG. 2.

INVENTOR.
CHARLES H. POOL

BY
Brown, Jenk & Synnestvedt

AGENTS

United States Patent Office

2,763,608

Patented Sept. 18, 1956

2,763,608

ELECTRO-CHEMICAL TREATMENT

Charles H. Pool, North Wales, Pa., assignor to Philco Corporation, Philadelphia, Pa., a corporation of Pennsylvania

Application June 23, 1953, Serial No. 363,523

2 Claims. (Cl. 204—143)

The invention hereinafter described and claimed has to do with etching and/or anodizing small articles. More particularly the invention is concerned with a method of uniformly treating predetermined surface portions of small articles, for example germanium crystals, by electrolytic techniques.

Since the process of the invention is particularly useful in electrolytic treatment of germanium crystals, the following description and the accompanying drawing are concerned with such an example. It should be understood that the electrolytic treatment may comprise either etching or anodizing operations, or both. These processes are substantially equivalent, for the purposes of this invention. The principles of the invention are also applicable to chemical etching of germanium crystals, or other small articles, as is referred to in more detail hereinafter.

In practising the invention I have first etched the crystals chemically, for example by use of a mixture of hydrofluoric and nitric acids, after which an electrolytic anodizing operation, utilizing antimony oxychloride as the electrolyte, was employed. The manner in which the invention applies to the last-mentioned procedure is described in detail below, and its applicability to chemical etching is also set forth.

For a number of reasons it is desirable to treat a predetermined face or surface portion of a germanium crystal device, usually the face which is to be contacted by the point electrode. The crystals are subject to deterioration resulting from chemical action taking place with contaminants present in the surrounding atmosphere, and it has been found that treatments of the kind contemplated, and particularly electrolytic treatment, stabilize the exposed surface and prevent such deterioration. Further, treatment of this kind insures that each of a plurality of crystals manufactured will have uniform electrical characteristics throughout its exposed surface. What change in the crystal is effected by the treatment is not precisely known, although a number of theories have been advanced. However, in any event, it is plain that the treatment is important and that beneficial results ensue.

Heretofore it has been difficult to control the stabilizing process, for example, the anodizing treatment, in such manner as to insure that successive crystals treated will be substantially alike. Satisfactory treatment of any predetermined portion of the surface of a germanium crystal requires controlled wetting of the crystal surface. In the practice of previously known methods it has been difficult to accomplish this. In prior practice the first step in the treatment was to bring the surface to be treated into contact with the electrolyte and, as has been stated, considerable difficulty has been encountered in effecting precise control of the amount of crystal area brought into contact with the fluid. Rather there was a tendency for the fluid to creep up the sides of the crystal and to wet varying surface areas. These difficulties have been encountered primarily because practice of the foregoing initial step has resulted in the formation of a negative meniscus in the surface of the treating fluid. This negative meniscus may break rather suddenly when the surface tension is overcome, with the result, as aforesaid, that the electrolyte flows up the sides of the crystals and may in some cases contact the structure which supports the same. When this occurs there is substantial variation in the area wetted, as between successive crystals being treated, and a corresponding variation in the current density through the individual surfaces which it is desired to treat. The necessity of avoiding such variations in current density will be appreciated when it is understood that, when such variations occur, successive crystals are not uniformly etched.

With the foregoing in mind it is, broadly, an object of the invention to provide a method whereby it is possible to wet predetermined surface portions only of an article to be treated, for example a single plane face of a germanium crystal.

More specifically the invention has as an object the provision of an improved method of stabilizing semiconductive crystals, the method being featured by the fact that any number of crystals may be uniformly treated on a successive mass production basis.

In accordance with these objects the invention includes, stated generally, the concept of first applying a small quantity of fluid to the surface to be treated, as for example by applying a drop which because of its surface tension wets only that surface, and thereafter causing relative movement between the surface and the treating fluid, as by lowering the crystal, until the mentioned small quantity of fluid which has previously wetted the surface makes contact with and merges with the electrolyte through which the treatment is effected. This condition is reached when the crystal is still spaced somewhat from the treating fluid, the initial wetting of the crystal surface resulting in formation of a positive meniscus extending between the electrolyte and said surface and making contact with the latter only. The pre-wetting prevents formation of the negative meniscus referred to, and the lack of control of the wetted area which has resulted. The treatment is concluded by subjecting the crystal to the requisite electrolytic operation.

In amplification of this brief description the invention is described below with detailed reference to a specific illustrative embodiment.

In the drawings:

Figure 1 is a partially diagrammatic view illustrating apparatus for carrying out the method of the invention; and,

Figure 2 is a fragmentary view showing a supported crystal adjacent the electrolyte, and illustrating the manner in which the positive meniscus bridges the gap between the upper surface of the electrolyte and the lower crystal surface which is to be treated.

With detailed reference to the attached drawing and initially to Figure 1 thereof, the numeral 10 designates an open top vessel partially filled with a suitable electrolyte 11, for example the antimony oxychloride referred to above. As the embodiment of the invention under consideration is concerned with the treatment of one face or surface only, of semi-conductors such as germanium crystals, a crystal of that kind is shown at 12 mounted by any suitable means upon a metallic stud 13 and conductively associated therewith. The crystal and the stud together comprise the anode of an electrolytic circuit which also includes the cathode shown at 14 and a source of electrical current 15, all connected in circuit by conductors 16 and 17 and through the agency of electrolyte 11. It will of course be realized that the

circuit is completed when the crystal is in contact with the electrolyte, as shown in Figure 2.

As pointed out above it is essential, for proper treatment of such crystals, that only the surface to be treated be in contact with the electrolyte. Heretofore the wetting action might vary, as respects successive crystals, under the influence of factors already described. As will now be appreciated, such variations resulted in corresponding variations in the current density through the crystal surface under treatment and has presented a substantial problem in controlling the degree of anodizing, or of etching if that technique be resorted to.

In particular accordance with the present invention these difficulties are overcome in the simplest possible manner, as is hereinafter described.

As shown in Figure 1 a small quantity or drop **20** of the electrolyte is applied to the lower surface of the crystal **12**, while the crystal is still spaced above the surface of the fluid. The drop **20** may be applied in any convenient manner, as for example by touching the crystal surface with a glass rod carrying a small quantity of the electrolyte, or by otherwise bringing the surface into momentary contact with a drop of suitable size. Due to the surface tension of the small quantity or drop **20** it does not spread beyond the flat, downwardly presented face of the crystal, with the result that only said face is wetted thereby.

The crystal is now lowered toward the surface of the electrolyte until the drop **20** just contacts the upper surface of the electrolyte, at which time the drop and said electrolyte flow together and form the small positive meniscus shown at **21** in Figure 2. Practice of the invention has shown that the upper surface of the enclosing meniscus is precisely co-extensive with the lower surface of the crystal, and for this reason the wetting action is limited to that surface only.

It will be appreciated that any suitable means may be employed to bring about the necessary relative movement between the crystal and the electrolytic fluid. One such means comprises the simple lever system shown diagrammatically in the drawing at **22**, although it is apparent that other means may be employed, it being necessary only that the apparatus be such as to enable precise movements of the crystal and to make it possible to stop the movement at the instant of formation of the positive meniscus.

In practicing the invention it has been found convenient to position a prismatic reflector **23** to one side of the receptacle **10**—the receptacle being transparent—and to observe the operation, as is indicated in Figure 1, in order to facilitate control thereof.

When the crystal has made contact with the fluid as described, the electrolytic circuit is completed and the treatment is initiated. The apparatus is controlled, either manually or automatically, in such manner as to discontinue treatment after a predetermined period of time sufficient to complete a stabilizing operation. Since only

the crystal surface under treatment has been wetted, it will be understood that flow of current takes place through said surface only, and it will further be appreciated that any number of semi-conductive crystals may be treated in accordance with this method, under controlled conditions assuring a uniform product.

As mentioned above, the concepts of this invention are also of utility as applied to purely chemical treatment of crystal surfaces. While no problem of current density is involved in such a procedure, it is nevertheless desirable to insure that the wetting action be limited to the surface under treatment, in order to prevent contamination of the crystal and undue etching of its lower peripheral edge. It is clear that pre-wetting of the surface, as by means of drop **20**, would result in controlled wetting in the chemical etching process.

While the principles of the invention have been described with specific reference to treatment of germanium crystals, it is to be borne in mind that such principles may be applicable to the treatment of a variety of small articles. However it will be understood that the field of the invention is defined by the scope of the appended claims.

I claim:

1. The method of electrolytically treating a single predetermined substantially planar surface of an article, which comprises: wetting only said surface of said article with a small quantity of electrolyte; bringing said small quantity of electrolyte into contact with the surface of a larger body of electrolyte to form a positive meniscus extending between the larger body of electrolyte and said surface, said meniscus making contact with only the mentioned surface of said article; and completing an electrolytic circuit through said surface.

2. The method of electrolytically treating a single substantially planar surface of a small body of semiconductive material, which method comprises: applying a drop of electrolyte to said surface, said drop of electrolyte wetting only said surface of said body; juxtaposing said body and a container of said electrolyte, with the mentioned surface confronting the electrolyte in said container; effecting relative movement between said body and the electrolyte in said container until the electrolyte comprising said drop merges with the electrolyte in the container and forms a positive meniscus extending from the electrolyte in the container upwardly into contact with only said surface of said body; and subjecting said surface to an electrolytic operation in which said body serves as one of the electrodes in the circuit.

References Cited in the file of this patent

UNITED STATES PATENTS

2,365,539	Flowers	Dec. 19, 1944
2,526,951	Kiefer	Oct. 24, 1950

FOREIGN PATENTS

373,398	Germany	Apr. 12, 1923