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SYNTHETIC STIBNITE CRYSTAL AND METHOD
FOR PRODUCING THE SAME
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FIG. 4

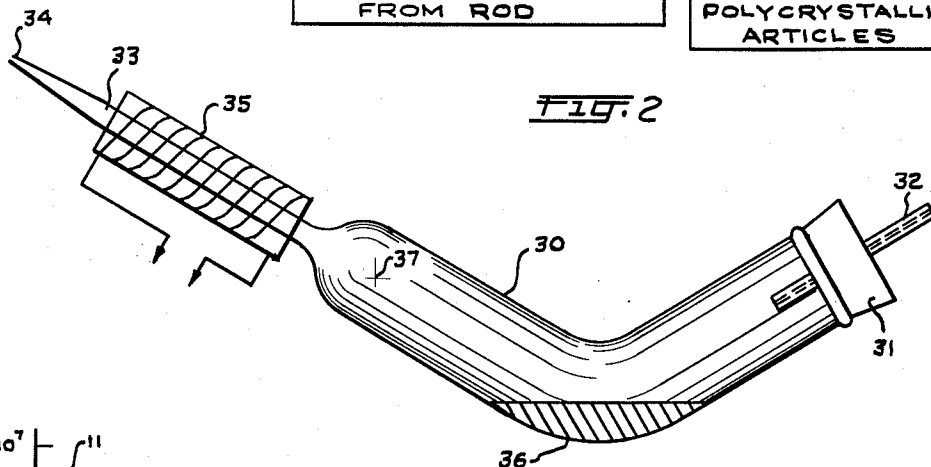
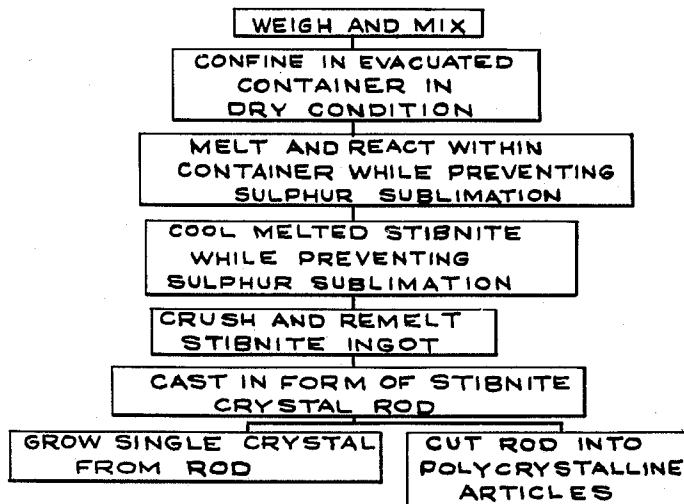


FIG. 2

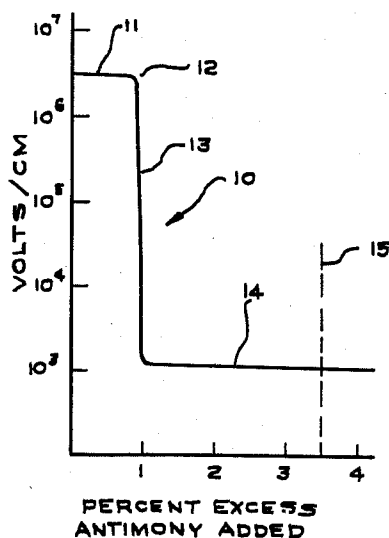


FIG. 1

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SYNTHETIC STIBNITE CRYSTAL AND METHOD FOR PRODUCING THE SAME

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11 Claims. (Cl. 338—22)

This invention relates generally to an improved stibnite composition of matter and to a method for producing the same. More particularly, it relates to an electric current controlling device in the form of a semi-conductor on-off device, or crystal switch.

As is known, stibnite occurring in nature is a high resistivity compound of antimony and sulfur (Sb_2S_3) which is poly-crystalline, brittle, and with a metallic luster. The resistivity of this naturally occurring compound is in the order of 10^9 ohm-centimeter, or higher, which resistivity value is commensurate with that of common electrical insulating materials. Concomitant with this high-resistivity characteristic, an electrical breakdown field of 10^6 volts per centimeter, or higher, is required before appreciable current flow takes place, when such a naturally occurring stibnite crystal, or vitreous form of such stibnite, is incorporated in an electrical circuit. This high value of electrical breakdown field is, of course, not suitable for use in ordinary electrical apparatus. It has now been discovered that these properties of stibnite are drastically modified when an excess of antimony is present in the material, and that a stibnite crystal synthesized to provide such excess antimony is well suited for use as a crystal switch.

An object of the invention is to provide an improved stibnite composition of matter.

Another object is to provide a synthetic stibnite crystal for use as a semi-conductor on-off device or crystal switch.

Another object is to provide a method for producing an improved stibnite composition of matter.

A further object is to provide a stibnite semi-conductor current control device which may be changed from a first stable operating condition to a second stable operating condition by means of a controlled electrical pulse.

Still a further object is to provide a stibnite semi-conductor current control device which may be changed from a second stable operating condition of relatively low resistivity to a first stable operating condition of relatively high resistivity by means of a controlled electrical pulse or by heating directly or indirectly.

The novel features believed characteristic of the invention are set forth in the appended claims. The invention itself, however, together with further objects and advantages thereof may best be understood by reference to the following description taken in connection with the accompanying drawings, in which:

Fig. 1 is a semi-logarithmic plot of electrical breakdown field versus percent antimony enrichment.

Fig. 2 is a chart indicating the processing steps employed in one satisfactory method for synthesizing the improved stibnite composition of matter.

Fig. 3 is a diagrammatic view of one form of apparatus, suitable for carrying out the casting of the remelted materials; and

Fig. 4 is a view indicating the compact size of a current controlling crystal switch made in accordance with the invention.

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As used herein, the term "crystal" is intended to signify both mono-crystalline and poly-crystalline forms of matter and the specific values of resistivity and electrical breakdown fields are to be interpreted as illustrative and not by way of limitation.

In accordance with the invention, a crystal of stibnite enriched in antimony to a value of between about 1.0% and about 3.5% by weight of the total weight of the stibnite composition of matter, is first prepared. This crystal is then formed to suitable size and shape and electrodes making a firm electrical and physical contact therewith, are provided. Thereafter, when incorporated in an electrical circuit having suitable means for applying heating; for applying a controlled radio-frequency field pulse; or for applying a controlled A.C. or D.C. field pulse, to the crystal, such crystal may be employed as a semi-conductor on-off device, or crystal switch.

Referring now to Fig. 1, it has been confirmed that when naturally occurring stibnite having the composition of Sb_2S_3 in stoichiometric proportions is subjected to an electric breakdown field, such field must be in the order of 10^6 volts per centimeter, or higher, before the breakdown occurs. Moreover, this relationship holds true with stibnite having an excess of antimony therein until that excess, or enrichment, reaches a value of about 1.0% by weight of such excess antimony based upon the total weight of the enriched material.

At or about this critical value, depending upon the purity of the ingredients, a surprising change in resistivity occurs, for when an electric field is applied to the stibnite having an enrichment of about 1%, there is a sudden large drop in resistance, resulting in a resistance breakdown when that electrical field reaches a value in the order of about 10^3 volts per centimeter. A voltage of this magnitude is, of course, practical for use in many forms of electrical apparatus. It further is found that this drop in resistance occurs in a duration-time of about a microsecond and that the resistance thereafter remains at its lower value until the crystal is subjected to further controlled treatment, as will later appear. Whereas the normal resistivity of the material is in the order of 10^9 ohm-centimeter, or higher, the resistance of the so-enriched material appears to be only about 10^3 – 10^4 ohms per centimeter under the application of the relatively low breakdown field which, for example, may be a controlled electrical pulse, either A.C. or D.C., and as applied by any conventional means incorporated in the circuit being served by the crystal switch.

The reason for this phenomenon is not known, but it has been observed that an electrically traceable low-resistance path through the material is formed upon the breakdown occurrence and which appears to be related to the position and influence of the excess atoms of antimony held in the stibnite lattice. Accordingly, the method for forming the synthetic material must provide for substantial homogeneity of the crystal which ultimately may be used as a crystal switch.

As further shown by the curve 10 in Fig. 1, the field required for breakdown of the material, generally maintains a high plateau value 11 until the critical value of antimony enrichment is present, as at 12. The abrupt drop in required field, as shown by 13, then levels off into another and lower plateau, as seen at 14, remaining in the order of about 10^3 volts per centimeter as the antimony enrichment is increased.

It further has been found that the crystal lattice of stibnite becomes saturated with excess antimony atoms in due time during the synthesis of the crystal, provided more than about 3.5% of excess antimony is present for reaction with sulfur. Thus, when a gross amount of antimony is present during that synthesis, the surplus antimony may not enter into the crystal lattice or may enter

therein in a non-homogenous manner. As shown, therefore, by the dotted line 15, the upper critical limit of enrichment is at about 3.5% enrichment depending upon the purity of the ingredients in the composition.

It has been found that although a synthetic stibnite crystal including excess antimony between the limits of 1% to 3.5% is satisfactory, the best results appear to be present when the excess antimony is between about 1.5% and about 2.5% and accordingly this is presently regarded as a preferred range of enrichment.

With the foregoing in mind, it will be apparent that the described characteristics of the synthetic stibnite crystal makes it well suited for use in automatically opening a circuit in many diverse kinds of electrical apparatus, as for example, circuits in digital computers or in other apparatus capable of being served by semi-conductors.

It further has been discovered that the described stibnite crystal will promptly have its original high resistivity restored when, after the breakdown field is removed, the crystal is subjected to heating. Such heating need be applied for only a few seconds time, preferably about 2 to 3 seconds, and need require only about 100° C. to 300° C. of temperature. Any conventional heating means (not shown) employed for heating small elements within an electrical circuit, may be used. Thus, when the original resistivity of the crystal is restored by such heating and the crystal again cools to normal temperature, it is well suited for use in automatically closing the circuit which it previously had opened. A single, small, sturdy piece of the stibnite crystal will serve both to open and close a circuit. As seen in Fig. 4, the crystal switch may comprise a round piece or wafer 20 about 2 mm. in diameter and with a thickness or length of about 10 mm., or less. To the faces of this wafer or crystal the circuit to be controlled is suitably connected as by a first lead 21 and a second lead 22, it being understood that depending upon the particular high-resistivity-restoring circuit employed, other leads or elements may also be attached to or placed in juxtaposition to the crystal switch. The leads 21 and 22 may, for example, be connected to the crystal by welding nichrome wires into the crystal through the use of a paste made of oil and powdered antimony telluride, or of silver or graphite paste; or by lead beads welded to the crystal; or by employing sharp spring-loaded metal electrodes.

In lieu of heating the crystal to restore its high resistivity, an electrical pulse, either A.C. or D.C., may be temporarily applied thereto by any conventional means incorporated in the apparatus employing the crystal or a radio-frequency field may be temporarily applied thereto by any conventional means in such apparatus.

As a feature of the invention, a method for producing the improved stibnite material also is provided. This method may be carried out in conventional apparatus, but experience has shown that satisfactory quality of the final product is largely dependent upon following the sequence of steps as herein disclosed. Referring now to the chart of Fig. 2, the sulfur and antimony are first carefully weighed, so as to provide the desired excess amount of antimony, and are then mixed in the chosen weight proportions. Commercially pure materials may be used and any suitable conventional weighing and mixing apparatus may be employed.

The prepared mix is then sealed inside a glass ampule which is evacuated after the mixture is placed therein and while also being suitably heated to drive off water vapor. Following this, the dry sealed materials are melted and reacted within that ampule by rotating the ampule in an electric furnace and with the reactants at a temperature of about 550° C., or higher. In order to prevent sublimation of the sulfur, the reacting materials are maintained in a constant state of agitation by the rotation of the sealed ampule during this reaction phase. At the conclusion of the melting and reacting phase, the molten stibnite having the ingredients mixed in a sub-

stantially homogeneous manner, is then slowly cooled and solidified, meanwhile continuing the rotation of the ampule during this cooling to insure against delayed sublimation of sulfur.

Thereafter the ampule is broken, the stibnite ingot is removed, and, if desired, may without further treatment, be cut into wafers for use as a poly-crystalline article. However, it is preferred to cast the irregular shaped ingot for more efficient usage and in so doing the following steps may be followed.

The ingot is crushed and the stibnite material then is carefully remelted at dull red heat and cast in a suitable apparatus, one form of which is diagrammatically shown in Fig. 3. As shown therein, the crushed ingot is loaded into a Pyrex glass vessel 30 which is provided at one larger end with a stopper 31 having a vent conduit 32 therethrough. At its other end the vessel has attached thereto, a glass tube 33 preferably of about 2 mm. in diameter and terminating in a capillary opening 34 at its distal end. This tube moreover is provided in its mid region with a suitable external heating coil 35.

Vessel 30 is suitably bent at its mid region 36 to provide a space of sufficient volume to hold the remelt contents prior to casting and is so mounted as to be selectively tipped about an axis represented at point 37, in order to direct the remelted material into the casting tube 33.

Upon being loaded in the vessel, the crushed ingot material is rapidly heated to its melting temperature as by means of a suitable torch applied to the vessel in the mid region 36. Upon being melted, the molten stibnite is promptly poured into the casting tube by tipping the vessel about the axis 37. The first of the material to reach the capillary open end of the casting tube promptly freezes in place, thus sealing and plugging that end of the tube and additional molten material deposited upon that frozen plug is maintained in flowable condition by heat supplied from coil 35 until all of the contents of the vessel 30 have been poured into the casting tube. Thereafter, heating from coil 35 is terminated leaving a solid cast rod of stibnite material in tube 33.

Upon thus forming the rod of cast stibnite which is in polycrystalline form, either of two procedures may be used. Firstly, the glass tube 33 may be broken from the vessel and destroyed, leaving a rod of polycrystalline enriched stibnite. In this case, the rod may be cut into wafers of suitable size and shape, for use as polycrystalline articles to which the electrodes may be attached. Secondly, the tube 33 containing the rod of stibnite may be broken at its proximate end from vessel 30 and sealed following evacuation of the open space in such tube by any conventional means. Thereafter the sealed tube with the cast rod therein may be placed in a conventional single-crystal-growing apparatus and dropped through a hot zone by a clockwork controlled motor at a rate of about one inch per hour, or less. After this crystal is grown, the mono-crystalline material is removed from the tube and is suitably subdivided to form a plurality of mono-crystalline articles to which electrodes may be attached.

While the invention has been described in both its mono-crystalline and poly-crystalline forms for use in a particular field, namely, the controlling of electrical currents, it will be understood that the novel stibnite composition of matter is not necessarily limited to such usage. Therefore, by the appended claims, it is intended to cover this material regardless of its particular usage or method of preparation.

What is claimed is:

1. As a new composition of matter, a stibnite crystal containing an excess amount of antimony comprising between about 1.0% and about 3.5% by weight of the total weight of the composition.

2. A crystal as defined in claim 1 and characterized by a monocrystalline form.

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3. A crystal as defined in claim 1 and characterized by a polycrystalline form.

4. A crystal as defined in claim 1 wherein the excess amount of antimony is between about 1.5% and about 2.5%.

5. An electric circuit element which comprises a stibnite composition in crystalline form containing an excess amount of antimony of between about 1.0% and about 3.5% by weight of the total weight of the composition, and electrodes making electrical and physical contact with said composition.

6. For use as a solid state switch in an electrical circuit, a stibnite crystal enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the crystal, said crystal being characterized by normally having a first stable operating condition of high resistivity in the order of about 10^9 ohm-centimeter when subjected to an electrical breakdown field of less than about 1000 volts per centimeter and having a second stable operating condition of low resistance in the order of about 10^4 ohm per centimeter when subjected to an electrical breakdown field of more than about 1000 volts per centimeter, said crystal being adapted to regain its high resistivity upon being heated to within the range of from about 100° C. to 300° C.

7. For use as a solid state switch in an electrical circuit, a stibnite crystal enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the crystal, said crystal being characterized by normally having a first stable operating condition of high resistivity in the order of about 10^9 ohm-centimeter when subjected to an electrical breakdown field of less than about 1000 volts per centimeter and having a second stable operating condition of low resistance in the order of about 10^4 ohm per centimeter when subjected to an electrical breakdown field of more than about 1000 volts per centimeter, said crystal being adapted to regain its high resistivity upon having a suitably controlled A.C. or D.C. field pulse applied thereto.

8. For use as a solid state switch in an electrical circuit a stibnite crystal enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the crystal, said crystal being characterized by normally having a first stable operating condition of high resistivity in the order of about 10^9 ohm-centimeter when subjected to an electrical breakdown field of less than about 1000 volts per centimeter and having a second stable operating condition of low resistance in the order of about 10^4 ohm per centi-

meter when subjected to an electrical breakdown field of more than about 1000 volts per centimeter, said crystal being adapted to regain its high resistivity upon having a suitably controlled radio-frequency pulse applied thereto.

9. The method of producing a substantially homogeneous stibnite crystal enriched in antimony and comprising, mixing antimony and sulfur to form a mixture enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the mixture, melting and reacting said mixture in a closed container to form a molten stibnite, cooling the molten stibnite to form an ingot, remelting the ingot, and casting the remelted ingot into a stibnite crystalline body of predetermined shape.

10. In a method of producing a substantially homogeneous stibnite crystal enriched in antimony, the steps comprising, mixing antimony and sulfur to form a mixture enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the mixture, melting and reacting said mixture in a closed container to form a molten stibnite and continuously agitating said mixture during said melting and reacting in order to prevent sublimation of sulfur from said mixture.

11. In a method of producing a substantially homogeneous stibnite crystal enriched in antimony, the steps comprising, mixing antimony and sulfur to form a mixture enriched in antimony by an amount comprising between about 1.0% and about 3.5% by weight of the total weight of the mixture, melting and reacting said mixture in a closed container to form a molten stibnite, cooling said molten stibnite to form an ingot, and continuously agitating said mixture during said melting and reacting and said molten stibnite during said cooling in order to prevent sublimation of sulfur from said mixture and from said molten stibnite.

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