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CRYSTAL CONTACT OF WHICH ONE ELEMENT IS MAINLY SILICON

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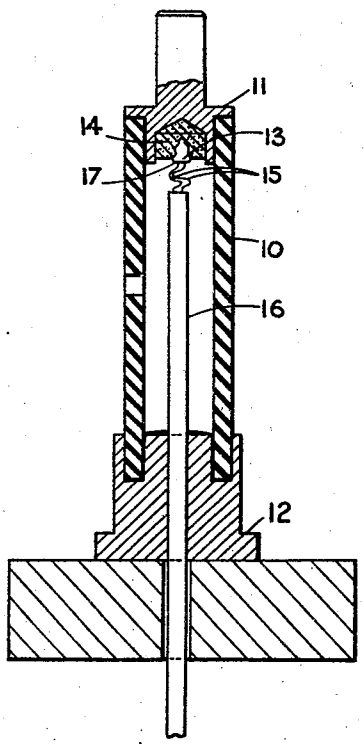


FIG. 1.

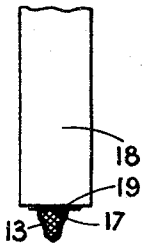


FIG. 2.

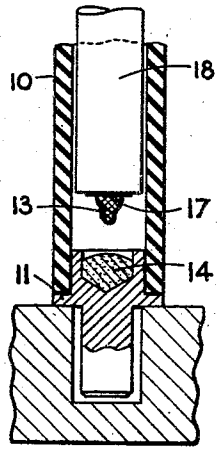


FIG. 3.

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CRYSTAL CONTACT OF WHICH ONE ELEMENT IS MAINLY SILICON

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11 Claims. (Cl. 250—31)

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This invention relates to electrical crystal contact devices of the type comprising a semiconducting crystal and a metal (usually a metal point) in contact with it. Such contacts can be used as rectifiers of alternating current or as "mixers," that is to say as non-linear impedances to which are applied an oscillation of frequency f_1 and another oscillation of frequency f_2, so that oscillations are produced having frequencies $(pf_1 \pm qf_2)$, where p and q are integers.

Objects of the invention are to provide improved processes for the preparation of the crystal in such contact devices, and crystal contact elements and wave-signal translating devices embodying such crystals that are more uniform or more efficient or both than those of the said type known hitherto. The uniformity aimed at means that the electrical characteristic of the contact should be as nearly as possible independent of the position on the crystal of a metal point forming the other element of the contact. Efficiency generally requires a high ratio of impedance in one direction (reverse impedance) to impedance in the other direction (forward impedance). It may also require that the absolute values of the forward impedance should be high or, alternatively, that they should be low. It may also require that the forward direction should be that in which positive charge flows from the crystal to the metal (positive contact) or that it should be that in which negative charge flows from the crystal to the metal (negative contact).

When the contact is used as a mixer, efficiency requires that the signal-to-noise ratio should be relatively high. Efficiency also requires that the performance of the contact judged by any of the foregoing criteria should deteriorate as little as possible with use or with age.

Silicon is one of the semi-conductors most widely used in crystal contacts. We have found that the said objects of the invention can be attained by introducing into substantially pure silicon a small proportion of aluminium or beryllium or both of these metals which form a solid solution with silicon and have extremely stable oxides. The term "small" implies that the ratio of the number of atoms of the additive metal to the number of atoms of silicon in the product is not greater than 1/50. Impurities, such as iron, which are often present in commercial silicon are generally undesirable and should be removed before the additive metal is introduced.

Crystal contact elements resulting from the herein disclosed process are the subject matter

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of divisional application Serial No. 736,094, filed March 20, 1947, and entitled Crystal contacts of which one element is mainly silicon.

If the starting material is the commercial silicon at present available, the introduction of the selected additive metal must be preceded by a purification. This purification can be effected by subjecting commercial silicon to the process described by N. P. Tucker in the Journal of the Iron and Steel Institute, vol. CXV(1), p. 412, 1927. This process removes only those impurities that are not contained in the silicon crystals, but occur as an additional phase, usually in the interstices between the silicon crystals. Commercial silicon is usually prepared by cooling a melt slowly; then practically all the deleterious impurities are in the interstices and can be removed by Tucker's process. If that process fails with any sample of silicon, it is probably because the silicon has been quenched rapidly; then the silicon should be re-melted and cooled slowly before it is subjected to the Tucker process.

The additive metal is preferably introduced by melting a mixture of the pure silicon and the additive. During this process care must be taken not to introduce undesired impurities. Those that might be derived from the air (a small quantity of oxygen is not necessarily deleterious) can be avoided by melting in a suitable atmosphere; the most suitable we have found is a vacuum, that is to say residual gas at a pressure of not more than 0.001 mm. of mercury. But it is difficult, or perhaps impossible, to find any crucible to contain the melt that does not react slightly with the melted silicon. This difficulty can be overcome by using a crucible consisting of or lined with pure beryllia; for then the only impurity introduced from the crucible is beryllium, which is not harmful but beneficial. It might be possible to introduce from the crucible all the additive metal characteristic of the invention; but in view of patent application Serial No. 446,310, filed June 8, 1942, we exclude from the scope of this invention any process of manufacturing the mainly-silicon element of a crystal contact which comprises only the steps mentioned in the claims of the specification of that application. If therefore the first step in the process consists in "grinding relatively impure silicon to a fine powder and treating it with chemical reagents so as to produce a relatively pure product," the process will not lie within the scope of the present invention unless part at least of the additive metal is derived from a

source other than a container in which the silicon is melted. But it is to be understood that the introduction of additive from the container is always to be taken into account when the amount of additive to be introduced from other sources is considered. Whether additive is or is not introduced from the container, that otherwise introduced may be aluminium or beryllium or a mixture of the two.

In order that the resulting crystals may have the best qualities, it is generally necessary and always desirable that, after the introduction of the additive, the crystals should be subjected to an appropriate treatment modifying their surface. One part of this process is a controlled oxidation; this part can be omitted only if the necessary oxidation has been effected during the melting or the cooling of the melt. We have occasionally succeeded in producing satisfactory results by this method; but it is difficult to control, and we greatly prefer to remove any surface oxide from the cooled melt with hydrofluoric acid and then to heat the product in a definitely oxidising atmosphere. Further we prefer not to attempt to produce the optimum surface oxidation by the heating alone; it is usually better to oxidise the surface somewhat more than is required and then to remove some (but not all) the layer of oxide with hydrofluoric acid.

Other surface treatments are also permissible and often desirable. Thus it is usually preferable to polish the fragments of the melt, or at least that part of them which is to contact with the metal point, before the controlled oxidation. Again, crystals are often soldered into metal capsules; then it is desirable to plate with metal that part of the crystal that is to lie in the capsule, in order that the solder may adhere to it.

One method of performing the invention will now be described by way of example, with reference to the accompanying drawings, in which:

Figure 1 shows the completed crystal contact device;

Figure 2 shows a silicon fragment temporarily mounted in readiness for a step in the process of preparation; and

Figure 3 illustrates the step of mounting the same element in a capsule.

Referring to Figure 1, the completed crystal contact device consists of a ceramic tube **10** capped at its ends respectively by a metal capsule **11** and a bush **12**. The crystal body **13** is set in the capsule **11** by means of a low-melting alloy **14**. One or more metallic contact elements **15** carried by a metal rod **16** co-operate with a prepared face **17** of the crystal body, the rod **16** being held fast in the bush **12**.

The starting material is commercial silicon which has been ground and passed through a 200 mesh sieve; the material contained the following metals in the following amounts reckoned as oxides: ($Al_2O_3+ZrO_2$) 1.01%, Fe_2O_3 0.96%, TiO_2 0.021%, MnO 0.08%, BaO 0.03%, CaO 1.13%, CuO 0.002%, MgO less than 0.002. In step 1 this material was purified by the aforesaid method described by Tucker. The resulting material had the following composition: ($Al_2O_3+ZrO_2$) 0.03%, Fe_2O_3 less than 0.005%, TiO_2 less than 0.0005%, MnO less than 0.001%, BaO less than 0.003%, CaO 0.008%, CuO 0.001%, MgO less than 0.002%, In step 2, the purified material is melted in vacuo (pressure less than 0.001 mm. of mercury) in a pure beryllia crucible, together with aluminium in an atomic proportion of 1 Al to 400 Si. The beryllia was fired to 1400° C., ground and washed with nitric acid before being made into a crucible.

In a further step 3 a fragment of the cooled melt has a plane part of its surface highly polished by any of the processes customary among metallurgists, for example grinding with emery of increasing fineness and finally polishing with alumina or magnesia or both. In a further step 4 the whole surface of the fragment is then dipped for 5 minutes into commercially pure 40% hydrogen fluoride diluted with an equal quantity of water. The main purpose of this treatment with hydrofluoric acid is to prepare the polished surface for the subsequent oxidation; accordingly it is not necessary, though it is usually convenient, that the unpolished part of the surface should be dipped.

In a further step 5 the necessary surface oxidation is performed. For this purpose the body resulting from step 4 is placed on a flat silica tray (together possibly with other bodies at the same stage of preparation) and introduced into a silica tube furnace filled with air at a region thereof maintained at 1050° C. There is a definite optimum temperature for this treatment, the temperature should be observed, e. g. by a thermocouple, and kept as near to 1050° C. as possible. The body is maintained in the said region for 2 hours and then allowed to cool. An atmosphere of oxygen at a controlled pressure may be substituted for the air in the furnace; then the time of heating will depend on the pressure of the oxygen.

In a further step 6 the treatment given in step 4 is repeated. Now part of its object is to prepare the unpolished part for step 7; accordingly the unpolished part must be dipped. In the process now being described in detail the dipping of the polished part is equally necessary, in order that part of the oxide layer formed in step 5 should be removed; but, as explained heretofore, it might possibly not be in a modification of the process. After the dipping, the body is washed with water.

In a further step 7 a metallic layer is deposited on some or all of the unpolished surfaces. The layer must not be deposited on the polished surface; accordingly, as shown in Figure 2, this is first protected by coating the flat end of a rod **18** with a layer of adhesive **19**, which may be the material known as monostyrene, and pressing the polished surface **17** of the body **13** against this layer. The exposed unpolished surface is then coated with copper by a method described by Bedel in Comptes Rendus, vol. 192 (1931), page 802. It consists merely in dipping the surface for 5 to 10 seconds into a solution of cuprous oxide in 20% hydrofluoric acid; the copper layer deposited may be subsequently thickened by electrolysis. Copper is not deposited on tungsten or molybdenum by this process; accordingly the rod **18** may be conveniently of tungsten or molybdenum. The coated surface is then washed and dried. The body can then be mounted in the metal capsule **11** by means of solder or some other suitable low-melting alloy intervening between the metal layer and the capsule. For this purpose the rod **18** is inserted in the tube **10** so that the crystal enters the molten alloy **14** in the capsule **11**, which is temporarily placed on an end of the tube. After the alloy has set, the rod **18** is detached from the body and the polished surface of the body cleaned from the adhesive by washing with a suitable solvent, such as benzene or ethyl acetate. The mounted crystal body is then ready

for final assembly into the structure shown in Figure 1.

A suitable metal element to co-operate with a crystal so prepared is the end of a tungsten wire 0.2 mm. in diameter, this end being sheared off along the cleavage plane which lies at about 45° to the axis of the wire. The pressure between the wire and the polished crystal surface may be 10–15 gm. weight. If the contact is tested with an applied D. C. E. M. F. of 0.7 volt, then, after little searching, a point can be found where the forward impedance is about 200 ohms, and the ratio of reverse to forward impedance is at least 30. With a lighter pressure a ratio of 100 or more can usually be obtained, but then the forward impedance is greater. The contact will usually stand without appreciable deterioration the passage across it, for a period of 10 to 60 secs., of a current (limiting current) of 40 to 80 ma. Comparable average figures for the commercial silicon that was the starting material, polished as described hereinbefore but not treated otherwise, are forward impedance 180 ohms, ratio of reverse to forward impedance 5, limiting current 5–20 ma.

If a lower forward impedance is required, the pressure between crystal and wire may be increased to 30–50 gm. weight. A forward impedance in the neighbourhood of 100 ohms can then be obtained, but the average ratio of reverse to forward impedance is likely to be 10–20, and the limiting current 30–60 ma.

If a high limiting current is not so important as the impedance characteristic, the aforesaid sheared tungsten point may be replaced by a fine tungsten point obtained by the well known process of etching with Langmuir's solution.

One advantage of crystals prepared according to the invention is that they are so uniform that it is often possible to locate two metal points ("whiskers") in parallel on the same crystal without adjusting them separately, as shown in Figure 1, and yet to obtain in this way an improved characteristic. The improvement is usually not so much in the impedance as in the limiting current that the contact will stand without deterioration. No novelty is claimed for the bare suggestion that whiskers on the same crystal may be connected in parallel; but, so far as we are aware, no disclosure has been made before how crystals might be prepared that are at once of high efficiency and also so uniform that the suggestion is practically useful.

We claim:

1. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the step of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon.

2. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the step of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon, a quantity of at least one of the two metals aluminium and beryllium, said quantity being such that the ratio of the number of atoms of said additive metal to the number of atoms of silicon in the product is not greater than 1/50.

3. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of adding to solid silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium also in solid form, and thereafter melting the mixture.

4. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of adding to solid silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium also in solid form, and thereafter melting the mixture in a container at least the interior surfaces of the walls of which are composed of pure beryllia.

5. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, and subjecting to a controlled process of surface oxidation the body of silicon into which said additive metal has been introduced.

6. In the manufacture of an electrical crystal contact device of the kind in which the semi-conducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, treating with hydrofluoric acid a surface of the body of silicon into which said additive metal has been introduced, thereafter heating said body in an oxidising atmosphere, and treating said surface again with hydrofluoric acid so as to remove some but not all of the oxide layer formed during said heating.

7. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, polishing part at least of the surface of the body of silicon into which said additive metal has been introduced, and subjecting to a controlled process of surface oxidation said polished part.

8. In the manufacture of an electrical crystal contact device of the kind in which the semiconducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free

from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, and coating with a metallic layer part of the surface of the body of silicon into which said additive metal has been introduced.

9. In the manufacture of an electrical crystal contact device of the kind in which the semi-conducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, polishing part of the surface of the body of silicon into which said additive metal has been introduced, affixing the flat end of a rod by means of an adhesive to said polished surface part, dipping said body into a solution of cuprous oxide in hydrofluoric acid, removing said rod from said body, and cleaning said surface part free from adhesive.

10. In the manufacture of an electrical crystal contact device of the kind in which the semi-conducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the

metallic impurities usual in commercial silicon a determinate small quantity of at least one of the two metals aluminium and beryllium, which additive metal forms a solid solution with the silicon, coating with a metallic layer part of the surface of the body of silicon into which said additive metal has been introduced, and mounting said body in a metal holder to which said metallic layer is soldered.

11. In the manufacture of an electrical crystal contact device of the kind in which the semi-conducting crystal contact element is mainly silicon, the production of said silicon contact element by a process which includes the steps of introducing into silicon that is substantially free from the metallic impurities usual in commercial silicon a quantity of additive metal such that the ratio of the number of atoms of said additive metal to the number of atoms of silicon in the product is not greater than 1/50, polishing a part of the surface of the body of silicon so produced, treating said polished part with hydrofluoric acid, thereafter heating said body in an oxidising atmosphere, and treating said surface again with hydrofluoric acid so as to remove only some of the oxide layer formed by said heating.

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