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CRYSTAL CONTACTS OF WHICH ONE ELEMENT IS SILICON

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This invention relates to electrical crystal contacts of the type in which an element is silicon; the other element is usually a metal point. Such contacts can be used as rectifiers of alternating current or as "mixers," that is to say 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 silicon elements of such crystal contact devices, and crystal contact devices embodying such silicon elements, 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 silicon 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). Hereinafter when impedance is mentioned without the qualification "forward" or "reverse," the forward impedance is meant. It may also require that the absolute values of the forward impedance should be high or, alternately, that they should be low. It may also require that the forward direction should be that in which positive charge flows from the silicon to the metal (positive contact) or that it should be that in which negative charge flows from the silicon 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.

This invention is based on the recognition that a very high degree of purity in the silicon of such a contact promotes the obtaining of uniformity and efficiency of performance of the contact. Effective purification of commercial silicon involves the step of grinding the silicon to a fine powder, and in this form the pure silicon is incapable of use in contacts, in which relatively large fragments are required. We have discovered that it is possible to use such a purification process without contaminating the silicon in the subsequent step of melting it to yield the necessary fragments, provided suitable precautions are taken.

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According to the invention, the manufacture of the silicon element of a crystal contact of the type specified comprises the steps (1) grinding relatively impure silicon to a fine powder and treating it with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon, (2) melting this pure product, out of contact with the atmosphere, and while contained by pure beryllium oxide.

No novelty is claimed for either of these steps per se; a novel feature of the invention lies in combining the two steps to form one stage in the manufacture of the silicon element of a crystal contact of the type specified.

In carrying out step (1) aforesaid we have found suitable the process described by N. P. Tucker in the Journal of the Iron and Steel Inst., vol. CXV (1), p. 412, 1927.

It is probably impossible to find any container for melted silicon that will not react at all with the silicon. But we have found containers of two kinds that react so little that, if the product is not retained in the container longer than is necessary to secure complete melting, they produce no contamination, that is to say, they introduce no impurity that is prejudicial to efficiency of the final contact. One of these containers is a crucible made of or lined with pure beryllium oxide. The other is a tantalum crucible coated with tantalum carbide by heating it to about 2000° C. in naphthalene vapour. It is important that the coating of carbide should be continuous, e. g., free from pin holes. We know of no reason why any other container should be used.

In order to melt the silicon the crucible may be heated by high frequency currents induced either in it (if it is of metal) or in a metal (e. g., molybdenum) cylinder surrounding it. As already indicated, the heating should be stopped as soon as melting is complete.

The character of the resulting contact depends to some extent on the gas in contact with the silicon during the melting. If a low impedance positive contact is required, the density of the surrounding gas is preferably negligible; e. g., the gas should be residual gas at a pressure of less than 10^{-3} mm. We have found that presence of a little oxygen in the surrounding gas is not always deleterious, especially if a negative, rather than a positive, contact is desired. However, the effects of oxygen are extremely complicated and have not been completely analysed.

The uniformity of the contact is often promoted by polishing the silicon where it is to contact with the metal, for example, by grinding it on emery cloth of increasing fineness and finally buffing it to a high polish. But occasionally it may be desirable to use the rough broken surface of the melt; for then a point is more likely to keep its position.

Substantial and sometimes desirable modifications of the properties of the silicon may be made by treating the surface, where it is to contact with the metal, with hydrofluoric acid, e. g., by immersing it for 10 seconds in a mixture of equal parts of pure hydrogen fluoride (40%) and water.

In the experiments whose results are given below the point associated with the silicon was the end of a tungsten wire, 0.2 mm. in diameter, sheared along the cleavage plane which is inclined at approximately 45° to the axis of the wire. The pressure between the point and the silicon was 10 to 15 gm. weight. The E. M. F. applied was 1.5 volts direct. The silicon was melted in a carbide-coated tantalum crucible.

If the point is in contact with a natural cleavage plane of the crystal, the effect of the acid is usually to decrease the impedance and to increase the aforesaid ratio, unless possibly that ratio is already high. Two examples of the effect are given in Table I.

Table I.—Natural cleavage surface

	Before HF treatment		After HF treatment	
Forward Impedance............ohms..	415	273	198	208
Reverse Impedance / Forward Impedance	2.5	15.5	12.7	18.9

If the point is in contact with a polished surface, the impedance is less affected; but the effect on the ratio is similar. Two examples are given in Table II.

Table II.—Polished surface

	Before HF treatment		After HF treatment	
Forward Impedance	233	264	245	238
Reverse Impedance / Forward Impedance	12.8	18.4	17.0	17.7

It should be mentioned that these effects of HF treatment are much greater than we have ever observed on commercial silicon.

An increase in the impedance without much (or any) decrease of the said ratio can sometimes be produced by treating a natural cleavage surface with an oxidising agent such as hot caustic alkali solution, e. g., by dipping it for 5 secs. into a boiling solution of 10 gm. caustic soda in 100 ml. water. Thus in one example the results shown in Table III were obtained.

Table III

	Before NaOH treatment	After NaOH treatment
Forward Impedance	210	933
Reverse Impedance / Forward Impedance	15.5	15.0

The effect of caustic soda on a polished surface appears to be less.

We claim:

1. In the manufacture of an electrical crystal contact device of the kind in which a contact element thereof is silicon, the production of the said silicon contact element by a process which comprises the steps (1) grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon, (2) melting the pure product of such treatment, out of contact with the atmosphere, and while contained by pure beryllium oxide.

2. In the manufacture of an electrical crystal contact device of the kind in which a contact element thereof is silicon, the production of the said silicon contact element by a process which comprises the steps (1) grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon, (2) melting the pure product of such treatment in the presence of residual gas at a pressure of less than 10^{-3} mm., and while contained by material with which said pure product does not react chemically in such a manner as to become contaminated undesirably, and (3) after solidification of said molten product oxidizing at least that face of said contact element which is to be engaged by the point contact element of said device.

3. In the manufacture of an electrical crystal contact device of the kind having two co-operating contact elements, one of said contact elements being of silicon, the production of said silicon contact element by a process which comprises (1) grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon, (2) melting the pure product of such treatment, out of contact with the atmosphere, and in a container of such a composition that said pure product does not react chemically with it in such a manner as to become contaminated undesirably, and after solidification of said molten product treating a natural cleavage surface thereof with hydrofluoric acid, and thereafter disposing the other of said contact elements in contact with said etched face.

4. In the manufacture of an electrical crystal contact device of the kind having two co-operating contact elements, one of said contact elements being of silicon, the production of said silicon contact element by a process which comprises (1) grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon, (2) melting the pure product of such treatment, out of contact with the atmosphere, and in a container of such a composition that said pure product does not react chemically with it in such a manner as to become contaminated undesirably, and after solidification of said molten product treating a face thereof with an oxidizing agent, and thereafter disposing the other of said contact elements in contact with said treated face.

5. In the manufacture of an electrical crystal contact device of the kind having two co-operating contact elements, one of said contact elements being of silicon, the production of said silicon contact element by a process which comprises (1) grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substan-

tially all the impurities usually present in commercial silicon, (2) melting the pure product of such treatment, out of contact with the atmosphere, and in a container of such a composition that said pure product does not react chemically with it in such a manner as to become contaminated undesirably, and after solidification of said molten product treating a natural cleavage surface thereof with a caustic alkali solution, and thereafter disposing the other of said contact elements in contact with said treated surface.

6. In the manufacture of an electrical crystal contact device of the kind having a silicon contact element co-operating with a metal contact element, the preparation of said silicon element by steps comprising grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon and melting the pure product of such treatment in a gaseous medium at a pressure of less than 10^{-3} mm. and in a container of such a composition that said pure product does not react chemically with it in such a manner as to become contaminated undesirably, and after solidification of said molten product, treating a natural cleavage surface thereof with an etching reagent, and thereafter disposing said metal contact in contact with said treated surface.

7. In the manufacture of an electrical crystal

contact device of the kind having a silicon contact element cooperating with a metal contact element, the preparation of said silicon element by steps comprising grinding relatively impure silicon to a fine powder and treating said powder with chemical reagents capable of removing substantially all the impurities usually present in commercial silicon and melting the pure product of such treatment in a gaseous medium at a pressure of less than 10^{-3} mm. and while contained by pure beryllium oxide, after solidification of said molten product, polishing a face thereof, and treating said polished face with an etching reagent, and thereafter disposing said metal contact in contact with said polished and etched face.

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