

Jan. 7, 1969

R. T. HEPPLEWHITE ET AL
PROCESS FOR INTRODUCTION OF OXYGEN VACANCIES IN
PEROVSKITE FERROELECTRIC CRYSTALS
Filed March 10, 1966

3,420,776

FIG. 1

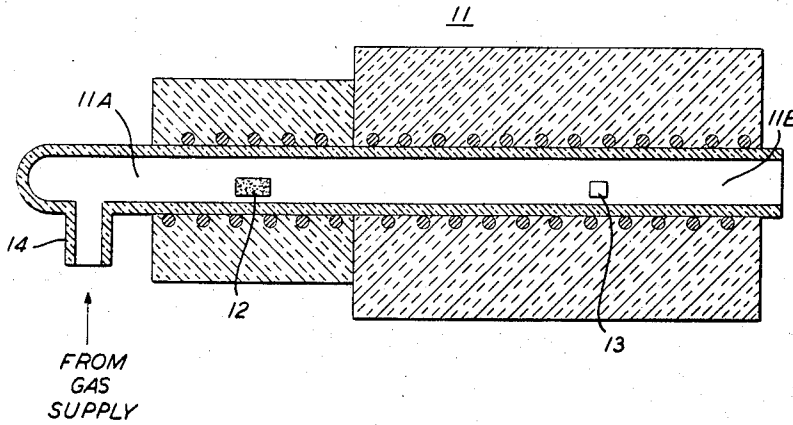
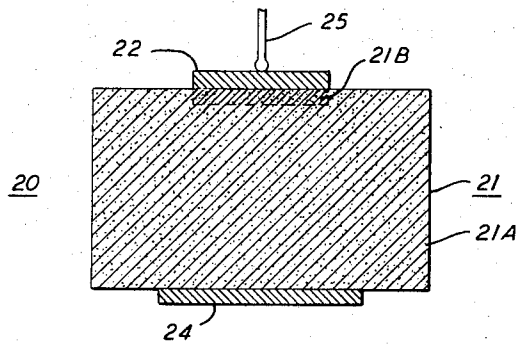


FIG. 2



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**PROCESS FOR INTRODUCTION OF OXYGEN
VACANCIES IN PEROVSKITE FERROELEC-
TRIC CRYSTALS**

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Filed Mar. 10, 1966, Ser. No. 533,175

U.S. Cl. 252—62.9

6 Claims

Int. Cl. C04b 35/50

This invention relates to ferroelectric oxide-type crystals and more particularly relates to the creation of oxygen vacancies in regions of such crystals whereby the conductivity characteristics of such regions are modified.

There has been a need for a method for creating oxygen vacancies in ferroelectric crystals of the perovskite type, such as potassium tantalate (KTaO_3), potassium niobate (KNbO_3), potassium tantalate-potassium niobate solid solutions (KTN) and barium titanate (BaTiO_3). Such oxygen vacancies act as donor sites to introduce free charge carriers in the crystal whereby it exhibits n-type semiconducting properties. By concentrating oxygen vacancies in localized regions of such a crystal, the crystal can be adapted to device applications. Moreover, the ability to introduce controllably oxygen vacancies to create donor centers can be especially useful when coupled with the ability to introduce controllably interstitial oxygen to create acceptor centers. A technique for the introduction of interstitial oxygen in crystals of the kind here of interest is described in copending application Ser. No. 419,138, filed Dec. 17, 1964, now Patent No. 3,323,947, of D. Kahng, J. R. Ligenza and S. H. Wemple assigned to the same assignee as this application.

However, it has proven difficult hitherto to introduce oxygen vacancies in localized regions of such crystals. In particular, the heating of such a crystal in a reducing or inert atmosphere to encourage the outdiffusion of oxygen from surface regions results in little outdiffusion but instead typically results in surface deterioration.

We have found experimentally, however, that the reluctance of the oxygen to diffuse out of the crystal can be substantially decreased by heating the crystal in an appropriate ambient, in particular in an ambient of the vapor of a metal such as calcium, which has the property that at the temperature to which the crystal is heated the free energy of formation of the oxide of such metal is larger in magnitude than that of the crystal. It is believed that such an ambient effectively lowers the surface potential barrier for oxygen, thereby permitting it to diffuse out of the crystal. The outdiffusion can be localized by covering surface portions where outdiffusion is to be avoided by a suitable mask, such as a layer of chromium.

The invention will be better understood from the following more detailed description taken in connection with the accompanying drawing in which:

FIG. 1 illustrates apparatus for carrying out the outdiffusion in accordance with one embodiment of the invention; and

FIG. 2 depicts a sectional view on a distorted scale of a typical device that can be fabricated by the practice of the invention.

With reference now to the drawing, FIG. 1 shows a furnace 11, essentially tubular in geometry, and including zones 11A and 11B which can be maintained at different temperatures. In zone 11A there is positioned a source 12 of the metal whose vapor is to be used to encourage the desired oxygen outdiffusion. In zone 11B is positioned the crystal or work piece 13 to be treated.

A carrier gas supplied from a suitable gas supply (not shown) is introduced by an inlet 14 at one end of the

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furnace for flow therealong past in turn vapor source 12 and work piece 13. At the opposite end of the furnace, the carrier gas can either be recovered or exhausted into the atmosphere. Argon has proved suitable for use as the carrier gas, although other gases, such as helium, which do not react unfavorably with other components of the system can be used.

As previously indicated, it appears that the effectiveness of the outdiffusion depends on the use of a vapor of a material having the ability to reduce the surface potential barrier which tends otherwise to impede the oxygen outdiffusion. Such materials include metals having the property that the free energy of formation of the metal oxide at the outdiffusion temperature is larger in magnitude than that of the work piece. In particular, calcium and samarium have proven particularly effective, although other divalent light metals and trivalent rare earth metals are expected also to be effective.

In typical runs involving calcium as the vapor metal, the temperature of zone 11A was kept at various temperatures between 870° C. and 1000° and the temperature of zone 11B between 600° C. and 1200° C. The temperature of zone 11A should be high enough to insure a high concentration of the calcium in the carrier gas. The temperature of zone 11B should be high enough that the diffusion rate of the oxygen in the crystal is adequate to achieve the desired outdiffusion in a reasonable time. As can be anticipated, the higher the temperature at which zone 11B is kept the faster and deeper the outdiffusion proceeds and the higher the temperature at which zone 11A is kept, the higher the concentration of oxygen vacancies at the surface.

In one specific example in which zones 11A and 11B were each kept at about 890° C. and 900° C. respectively, an oxygen vacancy concentration estimated to be about 4×10^{18} per cubic centimeter averaged in a surface region about 50 microns deep was created in thirty minutes in a crystal of potassium tantalate. In potassium tantalate-niobate and barium titanate the outdiffusion was found to proceed even faster.

Moreover, it has proven possible to prevent outdiffusion from particular surface regions simply by providing in intimate contact with such regions, a suitable mask. Such mask desirably is of a material which adheres well to the work piece, is convenient to apply and remove, and does not react unfavorably with other components of the system. Chromium in a layer about one micron thick has proved suitable for this purpose. Additionally, platinum has also proved effective, especially when there is first applied a thin titanium layer to improve adhesion. The titanium layer should be sufficiently thin so as not to absorb appreciable oxygen from the substrate.

An example of the devices to whose fabrication the invention is of interest is the microphone pickup 20 shown in FIG. 2. This microphone pickup basically is of the kind described in copending application Serial No. 467,211, filed June 28, 1965, by D. Kahng and S. H. Wemple and having the same assignee as the instant application. Microphone pickup 20 comprises a crystal 21 of potassium tantalate whose bulk 21A is n-type as the result of calcium doping of the melt from which it was grown. Additionally, the crystal is provided with a limited surface portion 21B which has been treated in the manner described above to create a high concentration of oxygen vacancies therein. This surface portion 21B can be formed in the manner described above, a chromium mask being used to define its area. This surface portion 21B characteristically may have a radius of about 10 mils and a depth of about 5 microns. Overlying surface portion 21B is a dot of gold 22 of a matching radius and a thickness of about 2000 Angstroms. As is described in the last-mentioned appli-

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cation, a gold contact overlying n-type potassium tantalate resulted in the formation in the crystal of a rectifying barrier which is pressure sensitive. Moreover, it has been found that this sensitivity can be enhanced if the portion of the surface of the crystal underlying the gold contact is treated to increase there the concentration of oxygen vacancies.

Ohmic connection to the bulk portion of the crystal is made by the deposition of a chromium layer 24 which advantageously is covered with a gold film to serve as a protective overlayer.

Pressure is applied to the rectifying barrier by means of a rounded stylus 25 in contact with gold dot 22. Typically, stylus 25 is connected to a sound pickup (not shown) which transmits incident sound waves to pressure on stylus 25.

It will be obvious that the principles can be extended to the fabrication of other devices.

What is claimed is:

1. The method of creating oxygen vacancies in a ferroelectric oxide crystal comprising the step of heating the crystal at a temperature at which the oxygen has a high diffusivity in an ambient of the vapor of a metal whose free energy of formation of the metal oxide at such temperature is larger than that of the crystal.

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2. The method of claim 1 in which the crystal is taken from the group consisting of potassium tantalate, potassium niobate, potassium tantalate-potassium niobate solid solutions and barium titanate.

3. The method of claim 2 in which the vapor is of a metal taken from the group consisting of calcium and samarium.

4. The method of claim 1 in which the crystal is potassium tantalate.

5. The method of claim 1 in which the crystal is potassium niobate.

6. The method of claim 1 in which the crystal is potassium tantalate-potassium niobate solid solutions.

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U.S. Cl. X.R.

23-51; 252-62.3, 520; 338-25