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D. KAHNG ETAL
METHOD FOR MAKING ELECTRODE CONNECTIONS
TO POTASSIUM TANTALATE-NIOBATE
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FIG. 1

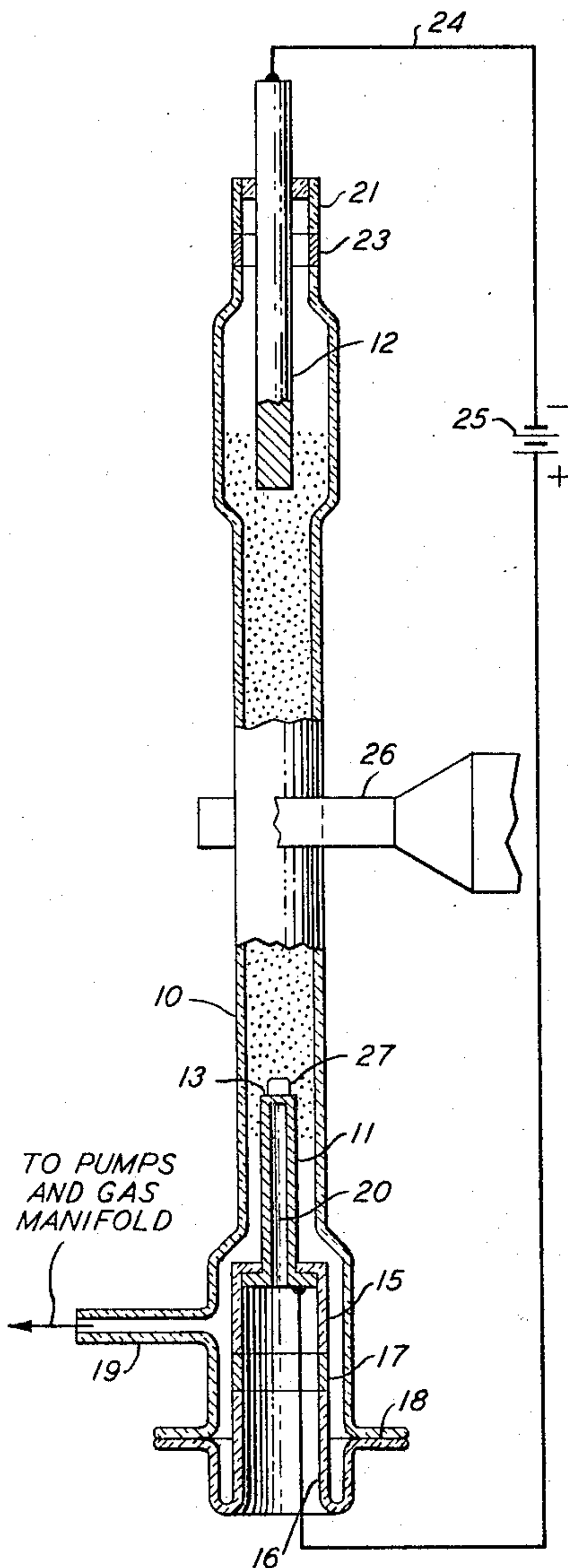


FIG. 2

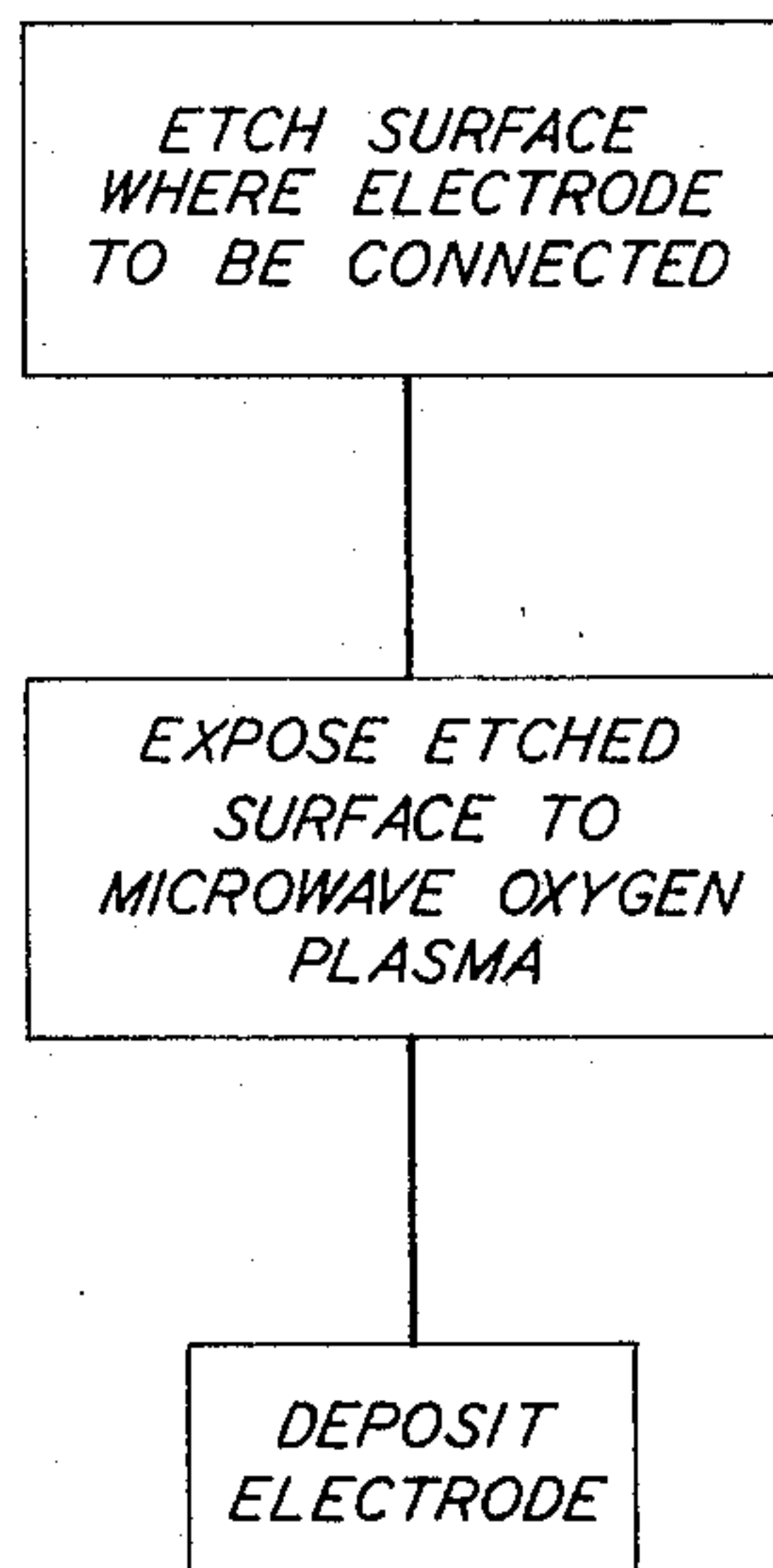
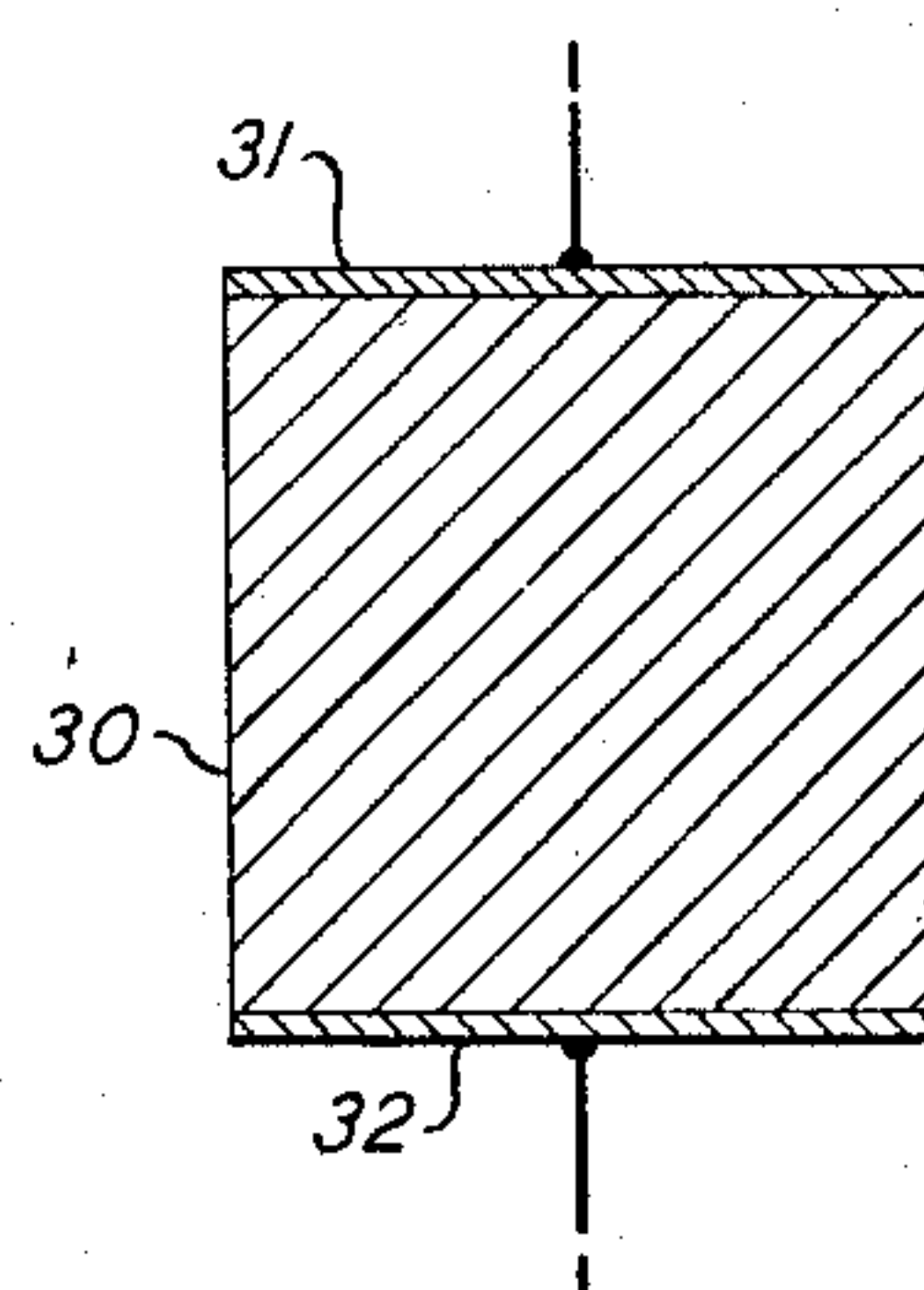


FIG. 3



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METHOD FOR MAKING ELECTRODE CONNECTIONS TO POTASSIUM TANTALATE-NIOBATE

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2 Claims. (Cl. 117-213)

This invention relates to the manufacture of devices utilizing compositions within the potassium tantalate-niobate system (hereinafter referred to as "KTN"). More particularly, this invention relates to the introduction of acceptor levels in a localized region of a KTN crystal.

As is described in copending application Ser. No. 353,049, filed Mar. 19, 1964, now Patent No. 3,290,619 (having a common assignee with this application), compositions included within the KTN system have properties which adapt them from various electrical applications, such as in electro-optic and electro-acoustic devices. These applications require the establishing of electro-static fields within the KTN element and, consequently, the attachment of electrodes to such element.

However, hitherto, optimum realization of the properties of KTN for such purposes has been penalized by the poor uniformity of the electro-static fields which have been achieved therein.

Accordingly, one object of the present invention is an improvement in the connections to a KTN crystal element whereby a more uniform electro-static field may be established therein.

In accordance with the invention, it is found advantageous for achieving a more uniform electro-static field within a KTN element to expose at least the surface portion where the connection is to be made to an oxygen plasma discharge, advantageously a microwave discharge, before the attachment of the electrode. Such exposure acts to make the surface more p-type. Such exposure has the effect of introducing acceptor levels in the regions affected.

Accordingly, when the crystal is p-type, this treatment acts to improve the ohmic nature of the contact. When the crystal is n-type, this treatment enables the making of a good rectifying connection to the bulk of the crystal. In each case, it is made possible to achieve a more uniform electro-static field in the crystal.

Although the invention has particular application to surface treatment of regions to which electrodes are to be attached, in a broader aspect the invention relates generally to the introduction of acceptor levels in a surface region of a KTN crystal independent of the purpose. For example, the invention has application simply to the formation in KTN crystal of junctions between regions of different conductivity type.

The invention will be more fully understood from the following more detailed description taken in conjunction with the accompanying drawing, in which:

FIG. 1 is an elevated and partly sectional view of typical laboratory oxidation apparatus suitable for treating the KTN element in an oxygen plasma in accordance with the invention;

FIG. 2 shows a flow chart of the basic steps of a process for forming electrical connections to a KTN crystal in accordance with the invention; and

FIG. 3 shows a KTN element to which electrodes have been connected.

With reference now more particularly to FIG. 1, the apparatus shown comprises a quartz discharge tube 10 of 1.3 centimeter inner diameter fitted at opposite ends with a pair of electrodes 11 and 12 separated by 30 centimeters. Electrode 11 is a hollow cylinder with a sealed

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end to provide a work surface 13. Electrode 11 is attached to a hollow cylinder of quartz 15 which is attached to a hollow cylinder of Pyrex glass 16 via a graded glass seal at 17. The whole electrode assembly is attached to one end of the discharge tube by a flange at 18. A gas line 19 is provided into the discharge tube from the vacuum pump (not shown) and to the oxygen gas manifold (not shown). The hollow inside of electrode 11 provides a well 20 for temperature measurement and/or for a coolant.

Electrode 12 extends out through a hollow cylinder of Pyrex glass 21 and the cylinder is attached to the discharge tube via a graded glass seal 23. Conductor 24 is attached to electrodes 11 and 12 and runs to a direct-current source 25. A microwave generator (not shown) supplies microwave energy to the resonant cavity 26 which is coupled to the discharge tube 10 for exciting a microwave discharge therein.

In general, the discharge tube and the electrodes can be of many materials. Quartz is a preferred material for the discharge tube because of its ability to withstand the high temperature of gas discharges. Silicon is a useful material for the electrodes because it has a low sputtering yield and can be readily degassed.

The tube dimensions and the parameters of the microwave assembly are variable over wide limits. What is important is that the assembly produce a sufficiently ionized discharge that will contact the KTN element 27 on the work surface 13.

The crystal to be treated in the apparatus described typically first needs to undergo some preliminary treatment. In particular, the individual elements, for example cubes with sides about 3 millimeters long, usually are cut from a larger crystal. This typically involves cutting with a diamond saw and grinding with alumina grit. The cutting and grinding operations generally result in a damaged surface layer which advantageously should be removed. One technique found convenient for removing the damaged surface layer involved immersion in molten potassium hydroxide at 350-400° C. for 10-20 minutes and subsequent washing in distilled water and drying. A wide variety of techniques are feasible for this preliminary step, so long as removal of the damaged layer is effected without adversely affecting the surface or introducing undesirable impurities. A beneficial side effect of this surface treatment is the elimination of crystal strains associated with the damaged surface layer.

After the described surface treatment, the KTN crystal is positioned on the work surface 13 of the anode element of the apparatus shown in FIG. 1 for exposure to the oxygen discharge.

It has been found convenient to operate the apparatus described with an oxygen pressure of about 0.3 millimeter of mercury initially in the discharge tube. In practice, it is found convenient first to evacuate the tube to approximately 10⁻⁶ Torr before admitting the oxygen gas. In some cases, it is found that the initial discharge has impurities such as CO, CO₂, and H₂O. If the gas is pumped out and the discharge established a few times, a relatively pure oxygen discharge can be obtained. Typically, a direct-current voltage of about 40 volts was established between the cathode and anode, resulting in a current flow of about 20 milliamperes. The discharge was initiated by applying about 300 watts of microwave energy at a frequency of 2450 megacycles. The KTN element was positioned on the holder so that the surface to be treated faced the cathode at the opposite end of the tube. Treatment of each of two opposite surfaces of the KTN element for ten minutes apiece was found adequate. It was estimated that the KTN element was heated to about 600° C. by the discharge.

Useful operating conditions were found to be variable over wide ranges without seriously effecting the results. The most significant parameter characterizing a glow discharge is its saturation current density. This fixes the number of ions striking the work surface in a given time interval. For the conditions described, the saturation current density was estimated to be about 25 milliamperes per square centimeter corresponding to about 200×10^{15} O_2^+ ions incident per square centimeter of surface per second. The energy of the oxygen ions incident was about 35 electron volts and penetration of about 3–5 Angstrom units was estimated.

The saturation current density which can be achieved varies with the frequency of the discharge and, accordingly, the time needed to introduce a prescribed number of oxygen ions will vary inversely with such frequency. In particular, it was found that when the discharge was established by applying energy of four megacycles' frequency, times of the order of hours were needed to achieve equivalent results. However, frequencies higher than several kilomegacycles do not result in any significant shortening of time. Actually, even at 2.45 kilomegacycles, substantially shorter times can be used with some slight sacrifice. The power supplied to the discharge need be no more than that necessary to ensure that the KTN element is in the region of the discharge. Shortening the length of the tube permits operation at lower power levels. The D.-C. voltage supplied also can be varied over wide limits. The voltage applied controls within limits the energy with which the oxygen ions bombard the KTN element and, accordingly, the depth to which they penetrate. Too low a voltage results in too low a penetration for optimum results; too high may result in undesirable disturbance to the KTN element. As previously indicated, the specific treatment described is estimated to introduce oxygen ions to a depth of between 3 and 5 Angstrom units. The oxygen pressure which can be employed is also subject to variation. However, if too low, there can be insufficient gas to absorb the radiation energy released by ionization and the radiation may damage the KTN element. If too high, the plasma can become too hot, with possible damage to the KTN element. A range of between .1 millimeter of Hg to about 5 millimeters of Hg is preferred. Moreover, instead of a closed discharge tube, it is feasible to flow the oxygen through a discharge region wherein the KTN crystal is supported.

The reason for the improvement effected by exposure to the oxygen discharge as described is not completely understood but appears to result from the filling of vacancies near the surface with oxygen ions.

After completion of the surface treatment described, there remains to attach the electrodes to the treated faces of the KTN element. This can be done in the same manner as disclosed in aforementioned application Ser. No. 353,049, now the said Patent No. 3,290,619, or in any

other fashion suitable to the desired electrode. Suitable electrodes can be of gold, aluminum and indium-gallium deposited by evaporation. Additionally, nickel electrodes have been deposited by the known electroless plating technique.

FIG. 2 shows in a flow chart the basic steps involved and FIG. 3 shows a KTN crystal 30 with a pair of electrodes 31 and 32 attached to opposite surfaces.

As is pointed out in the last-mentioned copending application, while the properties responsible for the device characteristics set forth therein are seen in a broad range of KTN compositions containing at little as about 20 percent of either of the end members $KTaO_3$ and $KNbO_3$, the present invention has applicability to the provision of electrode connections to the entire range of the system including compositions free of one of the two end members. Moreover, the principles are applicable even though the KTN element may include trace amounts of impurities either deliberately added or inherently present as a result of the single crystal growth process.

What is claimed is:

1. The method of preparing the surface of a crystal whose composition is within the potassium tantalate-niobate system comprising subjecting said surface to an etching process to remove damaged portions; modifying the molecular structure at and near said surface by mounting the crystal in proximity to an anode within a chamber containing said anode and a cathode; evacuating the chamber and establishing an oxygen ambient of between about 0.1 and about 5.0 millimeters of mercury pressure therein; applying a predetermined low direct-current biasing potential between said anode and cathode; creating an oxygen ion plasma in the crystal area by applying microwave energy to the chamber at such a location, at such a sufficient voltage, and at high enough frequency, as to cause a plasma-forming glow discharge to occur in the chamber such that the surface of the crystal is in the region of the discharge; and allowing the plasma to bombard the surface for a predetermined time.

2. The steps prescribed in claim 1 followed by the deposition of a metal electrode on said surface of the crystal.

References Cited

UNITED STATES PATENTS

2,750,541	6/1956	Ohl.	
2,787,564	4/1957	Shockley.	
2,883,544	4/1959	Robinson.	
2,902,583	9/1959	Steingerwald.	
3,146,514	9/1964	Knau	29—25.3
3,206,336	9/1965	Hora	148—1.5
3,212,939	10/1965	Davis	148—1.5

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