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J. P. REMEIKA
METHOD AND APPARATUS FOR PROCESSING
FERROELECTRIC CRYSTAL ELEMENTS
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2,777,188

FIG. 1



FIG. 3

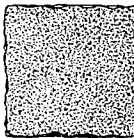


FIG. 2

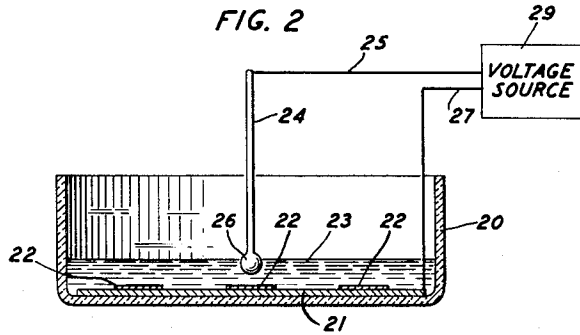


FIG. 4

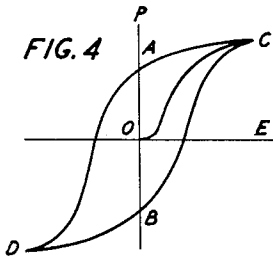


FIG. 5

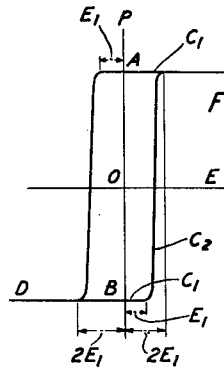


FIG. 6

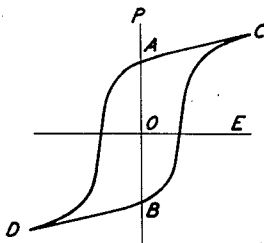
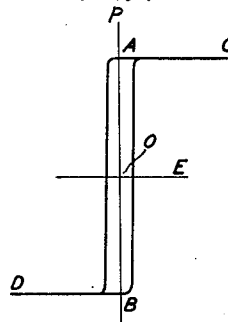


FIG. 7



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METHOD AND APPARATUS FOR PROCESSING FERROELECTRIC CRYSTAL ELEMENTS

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7 Claims. (Cl. 29—25.35)

This relates in general to the improvement of pulse storage units comprising ferroelectric crystals, and more specifically, single crystals of barium titanate.

Circuits used in certain types of digital computers, pulse storage, and switching devices feature, as their basic storage elements, crystals having properties known as ferroelectric. Such elements exhibit a relationship between applied electrical polarizing field and the resultant polarization which is similar to the hysteresis loop exhibited by magnetic materials.

It has been found that for optimum performance in the types of circuits mentioned above, the basic ferroelectric storage element should exhibit a hysteresis loop which is substantially rectangular, indicating a low coercive force, a high remanent polarization, and a high ratio between the charge storing capacities at different points in the cycle. These characteristics are best attained in single crystals of barium titanate, the electrical domains of which are substantially aligned in a single direction with respect to the "c," or optic axis of the crystal.

In preparing barium titanate crystals for storage application of the types mentioned, it is attempted during the growth process and by subsequent etching treatments to bring about a substantially unidirectional alignment of the electrical domains. Such a process has been described in detail in my application Serial No. 344,373, filed March 24, 1953 and in my article entitled "Growth of BaTiO₃ Single Crystals for Use as Storage Elements," Journal of the American Chemical Society, vol. 76, pp. 940, 941, February, 1954. Although crystals prepared in accordance with the aforesaid process have often been found to exhibit substantially uniform alignment of the domains, their characteristics are at times not entirely predictable in this respect, often because of strains existing in the crystal structure prior to treatment. Moreover, even when the optimum alignment is achieved during preparation, the domains are subject to misalignment during further handling and processing, such as is usual in dimensioning the crystal elements and applying electrodes.

Prior art treatments for the removal of misaligned surface domains by the use of chemically active etchants and strong electrolytes not only exert deleterious effects upon the crystal surfaces, but also invariably produce decompositional by-products which must later be removed. Further, it has been found impractical to immerse the treated crystals in the strong electrolytes of the prior art, inasmuch as this operation causes short-circuiting around the edges of the crystal, causing high current densities, with the possibility that the crystal will crack.

Accordingly, it is the principal object of the present invention to improve the domain alignment of ferroelectric crystal elements to facilitate pulse storage.

A more specific object of the invention is to improve the domain alignment in barium titanate crystal elements by a treatment which produces no deleterious effects on the treated elements.

A further object of the invention is to provide a treatment, characterized as above, which is adaptable for mass production techniques.

These and other objects, which will be apparent from a study of the specifications and drawings hereinafter, are attained in accordance with the present invention by placing a thin crystal wafer to be treated on a conducting metal plate and immersing the combination in distilled water. A field of between 2,000 and 3,000 volts per centimeter is applied across the thickness of the wafer, between the supporting metal plate and a conducting probe which is adjacent, but not in contact with, the upper surface of the wafer. In a preferred embodiment, to be described in detail hereinafter, the conductivity of the distilled water is about two micromhos per centimeter, the electrodes are platinum, and the frequency of the applied field 60 cycles per second, although the latter is not critical; in fact, direct current may be used. The field is applied for an interval of about two seconds, and then reduced to zero.

The technique of the present invention has been found to have the following advantages over prior art methods of ferroelectric domain alignment. (1) The distilled water does not react chemically with the crystal surface, and therefore does not cause deterioration thereof, or decompositional by-products which tend to form as deposits on the crystal surface. (2) Since, for the purposes of the presently disclosed treatment, it is unnecessary to apply solid electrodes to the crystal surfaces, the alignment of domains on the crystal surface remains relatively undisturbed. (3) There is no danger of the distilled water bath short-circuiting the edges of the crystal and hence, no danger of producing high current densities which might cause the crystal to heat up and crack during treatment. (4) Because of the simple form of the apparatus, the brief interval of treatment, and the absence of permanent connections with the treated element, the apparatus and techniques of the present invention are readily adaptable to mass production.

The present invention will be better understood from a study of the detailed specification hereinafter and the attached drawings, in which:

Fig. 1 is a view through a polarizing microscope showing the complex domain structure in a barium titanate crystal element prior to treatment in accordance with the present invention;

Fig. 2 is a cross-sectional view of a distilled water cell adapted for the treatment of ferroelectric crystal elements in accordance with the teachings of the present invention;

Fig. 3 is a view, similar to Fig. 1, of a barium titanate crystal element after treatment according to the present invention;

Fig. 4 show a hysteresis loop for a typical crystal of barium titanate;

Fig. 5 shows an ideal hysteresis loop for storage applications, and

Figs. 6 and 7 show hysteresis loops typical of crystal elements before and after the treatment of the present invention, respectively.

Applicant has disclosed in copending application Serial No. 344,373, filed March 24, 1953, and in his publication, hereinbefore identified, a technique for producing a ferroelectric crystal characterized by a low dielectric loss, low coercive force, high remanence, and a substantially rectangular hysteresis loop, which is adapted for use as a storage element in computer and switching applications. The crystals derived from the specific growth technique described in the foregoing application and in my cited publication consist of a principal component of barium titanate with small amounts of iron integrated into the crystalline lattice structure.

Many of the crystals grown in the manner described in my above application, when viewed through a polarizing microscope between a pair of polaroid films rotated for extinction, are found to be made up of a large number of bright and dark bands such as indicated, for example, in Fig. 1 of the drawings accompanying the present application. This is believed to be caused by the fact that part of the electrical domains are oriented with their optic axes at 90 degrees to the other domains. The bright bands represent *a* domains in which the optic axes are parallel to the major surfaces, causing these domains to exhibit birefringence in the thickness direction. The dark bands represent *c* domains in which the optic axes are perpendicular to the major surfaces, and hence, exhibit no birefringence in the thickness direction.

In order to provide a crystal having optimum storage characteristics, i. e., low coercive force, high remanence, and a substantially rectangular hysteresis loop, it is necessary that all of the domains be aligned so that the direction of easy polarization; that is, the "*c*" or optic axis, is perpendicular to the major faces of the treated crystal. This is accomplished in accordance with the present invention by applying a voltage in the thickness direction of a crystal element to be treated, while the latter is immersed in a bath of distilled water. The apparatus for performing this operation is shown in Fig. 2 of the drawings. It comprises a glass vessel 20 on the inside lower surface of which is disposed a platinum plate 21 which acts as a conductor. For illustrative purposes, applicant's novel treatment will be described as applied to square wafers two mils thick and seventy-five mils on a side, which, expressed in metric units, would be .05 millimeter thick and 1.9 millimeters on a side. These wafers are cut from single crystals of barium titanate prepared in the manner described in detail in my above-mentioned copending application Serial No. 344,373, and in my publication, and etched with phosphoric acid prior to the present treatment. The crystal wafers 22 to be treated are placed on top of the plate 21 in the vessel 20, which is filled with distilled water 23 to a level several millimeters above the upper surface of the crystals 22. A short piece of platinum wire 24, attached to a flexible lead 25, serves as a second conductor, disposed adjacent the upper surface of the crystal 22 under treatment. The platinum wire 24 terminates in a spherical probe 26 having a radius of about a millimeter, which is positioned about a millimeter above the center of the upper surface of crystal 22. The reason for using platinum for both the probe 26 and the base plate 21 is that platinum is chemically inactive, and hence, does not contaminate the distilled water bath. The probe 26 and the base conductor 21 are connected by leads 25 and 27 across a potential source 29 adapted to supply a potential of between say, 2,000 and 3,000 volts per centimeter of the thickness of the treated crystal. For convenience, one may use a potential source having a frequency of 60 cycles per second. However, the frequency is not critical, and even direct current can be used successfully. Although some of the field energy is lost through the water, enough charge appears on the surface of the crystal to effect orientation. Most effective operation was observed when the conductivity of the distilled water 23 was not greater than 2.1 micromhos per centimeter. The treated crystal 22, after being removed from the bath 23, was again observed under the polarizing microscope in the same position as prior to treatment, and between polaroid films set for extinction. It was found that a crystal wafer, subsequent to treatment for an interval of a few seconds, presents an almost entirely dark appearance, as indicated in Fig. 3 of the drawing, the *a* bands being no longer observable. This indicates that the electrical domains are in nearly perfect alignment throughout the entire wafer.

Referring now to Fig. 4 of the drawings, a hysteresis loop is shown which is typical of that produced by 60

cycles per second alternating voltage applied across an untreated barium titanate crystal. The electrical field strength *E* applied through the thickness of the crystal is plotted against the consequent polarization.

Starting from zero field and polarization at point O, the curve rises to the right, at first gradually, then rapidly, and finally slopes asymptotically to saturation at C. Removal of the positive field now allows the polarization to fall to a positive value at A, which is called the "remanent polarization." To reduce the latter to zero, a negative field must be applied, which is known as the "coercive force," the magnitude of which depends on the pretreatment of the crystal. By analogy to the hysteresis loop of ferromagnetic materials, the remainder of the complete loop CADBC is obtained.

Referring now to Fig. 5, an ideal hysteresis loop is shown for a material suitable for switching or computer applications such as, for example, memory cells of the type described in J. R. Anderson application Serial No. 254,245, filed November 1, 1951, now Patent 2,717,372, issued September 6, 1955. It should be noted that the fundamental requirement for such a material is that it be subject to electrical saturation by voltage pulses $\pm 2E_1$ volts; but when the ferroelectric material is in either state A or C, as indicated in Fig. 5, the application of voltage pulses of $\pm E_1$ volts will not be sufficiently high to change its final state. The capacitance of a single ferroelectric memory cell, which is represented by the slope of the hysteresis curve at any point, should thus always remain at a low value C_1 when positive or negative voltage pulses no higher than E_1 are applied. However, when positive or negative voltage pulses as high as $2E_1$ volts are applied in a direction to reverse internal polarization, the state of the ferroelectric material should pass rather abruptly from a low capacitance region C_1 to a high capacitance C_2 and then on to a low capacitance C_1 near saturation.

Assuming a 60 cycle voltage were impressed across the crystal shown in Fig. 1, which was in accordance with the teachings of my copending application Serial No. 344,373 and of my cited publication and etched in phosphoric acid, but prior to orienting treatment in accordance with the present invention, the resultant hysteresis loop appearing on the oscilloscope screen would assume the form shown in Fig. 6 of the drawings, in which polarization is plotted against applied voltage. After applicant's distilled water orienting treatment, the crystal is characterized by a rectangular hysteresis curve of the type shown in Fig. 7, which is the result of the nearly complete elimination of *a* domains. It is apparent from the showing that in the typical case, the voltage required for saturation is markedly decreased, as is also the coercive force, whereas the remanent polarization is significantly increased.

The following table shows ranges of parameter values for typical crystals tested.

SINGLE CRYSTALS OF BARIUM TITANATE AFTER GROWTH IN POTASSIUM FLUORIDE FLUX AND ETCHING WITH H_3PO_4

	Before Distilled Water Orienting Treatment	After Distilled Water Orienting Treatment
Coercive Force, Volts Per Centimeter.....	2,000-5,000	500-1,000
Saturation Field Strength, Volts Per Centimeter.....	10,000-25,000	700-1,500
Remanent Polarization, 10^{-6} Colombs Per Centimeter.....	8-10	26
Ratio C_1/C_2	50-80	1,500-5,000

It is to be understood that the figures given above are indicative of the effectiveness of applicant's treatment in typical cases, the degree of improvement depending to a large extent on the initial condition of the treated crystals, such as, for example, the presence or absence of strains and impurities in the crystal lattice.

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Although some of the foregoing values may be approximated by the methods set forth in my earlier filed co-pending application Serial No. 344,373, the presently disclosed technique has certain advantages in addition to those discussed earlier in the specification. An important one of these is that the resultant domain alignment is substantially uniform over the entire treated element, as is apparent from Fig. 3. This contrasts with the condition of the crystal element after prior art treatment in which only certain portions are in alignment, thus producing a marked variation in the hysteresis characteristics as the electrodes are moved from one point to another over the surface.

Although a specific apparatus has been disclosed by way of illustrating the principles of the present invention, it will be apparent to those skilled in the art that other forms may serve suitably for the practice of the present invention. Moreover, although the present procedures were specifically described with reference to treatment of barium titanate crystals grown by the method set forth in applicant's application Serial No. 344,373 mentioned above, it will be apparent that the method and apparatus are applicable also to the processing of other ferroelectric crystal elements prepared by any of the various known techniques.

What is claimed is:

1. An apparatus for uniformly orienting the domains in ferroelectric single crystal elements which comprises in combination, a bath of distilled water, and means including a pair of electrodes, which are chemically inert with respect to distilled water, disposed in said bath to direct an electrical field in the thickness direction of a crystal element under treatment of an intensity to align a major portion of the domains of said crystal in said thickness direction.

2. An apparatus for uniformly orienting the domains in ferroelectric single crystal elements which comprises in combination, a bath of distilled water having a conductivity not greater than approximately two micromhos per centimeter, and means including a pair of electrodes, which are chemically inert with respect to distilled water, disposed in said bath to apply an electric field of between

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2,000 and 3,000 volts per centimeter across the thickness of a crystal element under treatment.

3. An apparatus in accordance with claim 2 in which the electrodes of said pair comprise a flat plate for supporting the crystal element under treatment and a spherical probe spaced apart slightly from the upper surface of said crystal element.

4. An apparatus in accordance with claim 3 in which said electrodes are platinum.

5. A method for uniformly aligning the domains in a ferroelectric crystal element which comprises immersing said element in a distilled water bath and while said element is immersed in said bath directing a field in a thickness direction in said element which is of an intensity to align a major portion of the ferroelectric domains of said crystal in said thickness direction.

6. A method for uniformly aligning the domains in a ferroelectric crystal element which comprises immersing said element in a distilled water bath, and while said element is immersed in said bath directing an electrical field of between 2,000 and 3,000 volts per centimeter in a thickness direction in said element.

7. An apparatus for uniformly orienting the domains in ferroelectric single crystal elements which comprises in combination, a bath of distilled water having a conductivity not greater than approximately two micromhos per centimeter, a pair of chemically inert electrodes disposed in said bath comprising a plate adapted to support one of said elements under treatment, and a conducting probe located centrally with respect to the upper surface of said one element and slightly spaced apart from said surface, and a potential source connected across said electrodes and adapted to impress between 2,000 and 3,000 volts per centimeter across the thickness of the treated crystal element.

References Cited in the file of this patent

UNITED STATES PATENTS

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