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ZINC OXIDE MAXIMUM EFFICIENCY LENGTH EXTENSIONAL CRYSTALS AND DEVICES

Filed Oct. 25, 1966

FIG. 1

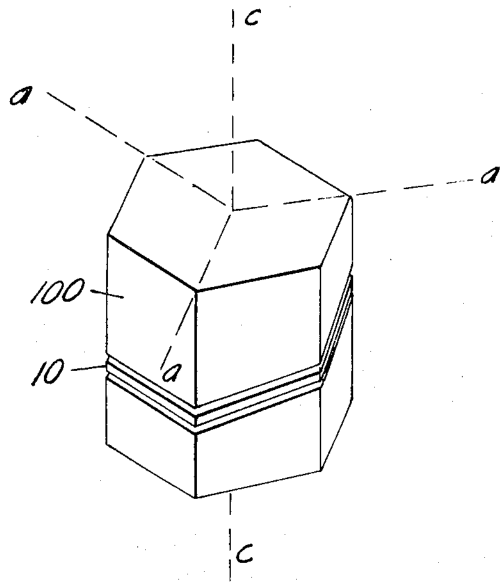


FIG. 2

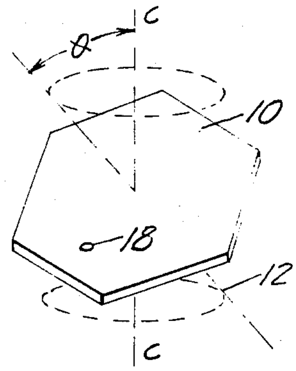


FIG. 4b

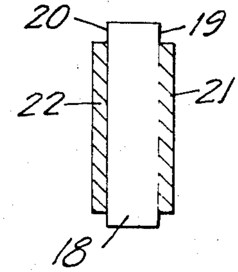


FIG. 4a

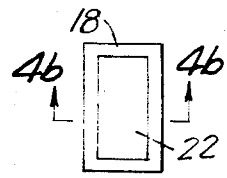


FIG. 3

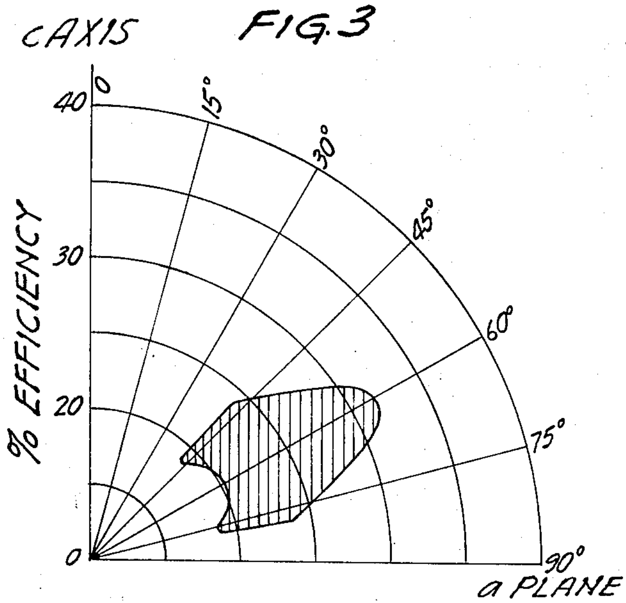


FIG. 5

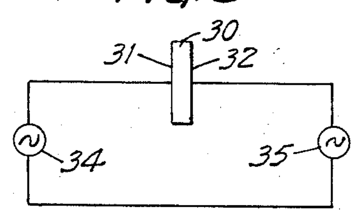
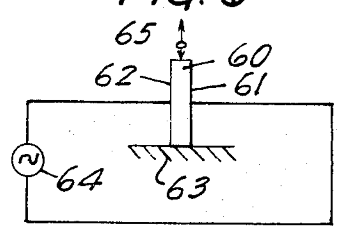


FIG. 6



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ZINC OXIDE MAXIMUM EFFICIENCY LENGTH EXTENSIONAL CRYSTALS AND DEVICES

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U.S. Cl. 310—9.5 7 Claims

ABSTRACT OF THE DISCLOSURE

A piezoelectric device is shown comprising at least one element which comprises of a piezoelectric zinc oxide crystal having an axis passing through the crystallographic *c*-axis and inclined at an angle theta relative to such crystallographic *c*-axis wherein theta ranges from about 42° to 78° and wherein the crystal has a resistivity between about 0.1 and 10^{12} ohm-cm., and means for making electrode contact with said element on at least one face.

This invention relates to zinc oxide crystals which are capable of propagating length extensional mode with an associated unexpectedly great and heretofore unrealizable electromechanical conversion efficiency, and to the improved devices made therefrom.

Zinc oxide, like quartz, is known to exhibit piezoelectric properties and to have excellent physical and chemical stability. Zinc oxide crystals exhibit the hexagonal Wurtzite lattice structure with the oxygen ions arranged in closest hexagonal packing and the zinc ions occupying half of the tetragonal interstitial positions. Characteristically, the Wurtzite atomic lattice structure has a crystallographic *a*-plane and a crystallographic *c*-axis. W. G. Cady in his book "Piezoelectricity" (published by McGraw-Hill Book, Inc., revised edition, 1964), gives the elastic and piezoelectric constants for this crystal class and describes the piezoelectric modes present for the crystallographic axes.

Heretofore, it was known that zinc oxide single crystals were capable of propagating length extensional modes if such crystals were electroded on faces perpendicular to the *c*-axis and parallel to the *a*-plane. However, the electromechanical conversion efficiency of acoustic length extensional modes so generated is less than about 20%.

I have now discovered, however, that zinc oxide single crystals formed with certain new crystal orientations have coupling coefficients of acoustic length extensional mode that greatly exceed the characteristic values obtained for those generated along the crystallographic *a*-plane. The fact that these new orientations can be used for generating such efficient modes is unexpected and surprisingly advantageous since most electromechanical device properties are considered by those skilled in the art to depend upon the square of such coupling coefficients.

The present invention is better understood by reference to the following attached drawings taken together with the associated specification:

FIGURE 1 is an isometric drawing illustrating a section of a crystal of the present invention;

FIGURE 2 is an isometric view of the crystal shown in FIGURE 1 and illustrating the angle θ;

FIGURE 3 is a two-dimensional plot in polar coordinants showing the relationship between θ and the percent efficiency (coupling coefficient) for a crystal of the invention;

FIGURES 4A and 4B illustrates one embodiment of a device of the invention formed from a crystal of FIGURE 2;

FIGURE 5 illustrates schematically one embodiment of a resonate cavity constructed using a device of FIGURE 4; and

FIGURE 6 illustrates schematically one embodiment of a quarter wave length transducer constructed using a device of FIGURE 4.

Referring to FIGURE 1 there is seen a section of a large single crystal of zinc oxide which is designated in its entirety by the numeral **100**. Such a crystal can be grown by any one of the known processes for the production of single crystal zinc oxide. This crystal **100** is seen to have a crystallographic *c*-axis and to have three crystallographic *c*-axes which together define a crystallographic *a*-plane.

A crystal wafer **10** of the invention can be made by any convenient procedure. For example, such a wafer **10** can be prepared from a crystal **100** by making two spaced parallel cuts through the crystal **100**, as follows: The crystal **100** is mounted conveniently on a conventional orientation jig (not shown) using wax or the like. An initial cut (not shown) is made approximately along a crystallographic *a*-plane near one end or tip of the crystal using a precision wafering machine. This cut tip serves as an orientation guide by subjecting such tip to an X-ray crystal orientation procedure to determine the true direction of the *c*-axis.

Next, the position of the orientation jig with the crystal mounted therein is carefully adjusted relative to the direction of cut by the blade in the precision wafering machine. One angle selected in this orientation process is the complementary angle to an angle theta (θ) (see FIGURE 2). Theta is the angle formed between the crystallographic *c*-axis and the axis **12** of wafer **10**. The cut crystal axis **12** passes through the crystallographic *c*-axis and is normal (or orthogonal) to the wafer **10** surface. Theta is measured relative to the crystallographic *c*-axis. In accordance with this invention, values for the angle theta range from about 42° to 78° and, thus, the complementary angle chosen ranges from about 12° to 48°. This relationship between the crystal axis **12** and the crystallographic *c*-axis conveniently describes what is herein termed the AM series of crystal shapes (see FIGURE 3).

A first preferred range of angles for theta in the AM series is from about 55° to 67° crystals because with these angles, crystals of the invention display maximum acoustic length extensional mode electromechanical coupling efficiency. A most preferred angle for theta, but one within the AM series, is about 60° because with this angle, a crystal displays greatest acoustic length extensional mode coupling efficiency.

In such AM series, the electric field propagation direction is required to be at an angle theta to the crystallographic C-axis and to be parallel to such crystal axis **12** in order to obtain the indicated unexpected acoustic wave generation in accordance with the teachings of this invention. Reference to FIGURE 3 is helpful in determining the optimum relationship between the coupling efficiency and the angle theta in a given crystal. FIGURE 3 indicates the magnitude of the improved coupling achieved in a crystal constructed using the AM series in accordance with the teachings of this invention.

Continuing on with this example of preparing a wafer **10** from crystal **100**, if the initial cut through crystal **100** happened to have been made, for example, at an angle θ which is outside the X-ray machine range, it is sometimes desirable to make a second cut through crystal **100** after the jig has been duly positioned as described. However, after a satisfactory initial cut has been made, and after the crystal **100** in this jig has been thus fixed relative to the cutting direction of the blade in the wafering machine, the orientation jig is advanced a convenient distance, typically ranging from about one-half to four millimeters. A second cut through the crystal **100** is then made so as to separate and define the desired crystal wafer **10**. The actual thickness of a crystal wafer **10** is correlated to the end use to which the wafer is to be placed, in accordance with the teachings of this invention, and as hereafter more fully described.

The resulting crystal wafer **10** is preferably subjected to a conventional doping operation (see, for example, the doping procedures described by G. Heiland, E. Mollwo and F. Stockmann in "Solid State Physics," vol. 18, pp. 191–319, 1959). If the crystal wafer **10** does not already have a resistivity value between about 0.1 and 10^{12} ohm-cm., the crystal resistivity may be adjusted to a value within this range during the doping operation, the exact resistivity value for any given crystal wafer **10** being dependent upon the particular properties desired for the end use intended.

The resulting doped crystal wafer **10** is now conveniently subjected to a mechanical or chemical polishing operation whereby its opposed faces are polished to a predetermined desired extent, care being exerted to maintain the crystal orientation. Those skilled in the art will appreciate that smooth facial surfaces are desirable in electroding and in subsequent device performance.

Thereafter, the crystal wafer **10** is available for electroding or for mounting in a device. For example, referring to FIGURE 4, there is seen a crystal wafer **18** which has been conveniently formed from a crystal wafer **10**, by means of an ultrasonic cutter, grinder, chemical etch bath, or the like. Part A of FIGURE 4 represents a top plan view of wafer **18**, while part B thereof represents a vertical sectional view thru wafer **18** taken along the line *b—b* of FIGURE 4A. The two opposed parallel faces **19** and **20** of the crystal wafer **18** have been appropriately masked and subjected to a vacuum vapor deposition operation so as to form thereon metal electrodes **21** and **22**. The use of vapor deposited electrodes is illustrative only, any any suitable method of forming electrodes on a crystal wafer **18** (such as electrolytic or electroless plating, sputtering, conductive pastes, and the like) can be used.

Parallel faces are used on crystal **10** for illustrative purposes only. It is sometimes advantageous to use crystals of this invention having nonparallel faces, or to use crystals of this invention with nonaligned or nonparallel electrodes, or to use such crystals with a plurality of such faces and such electrodes to control production of particular acoustic waves or to control desired electric field propagation. Such constructions and other equivalent ones are within the teachings of the present invention. It will be appreciated that a crystal of the invention can be formed with any desired geometry so long as the angle theta is described.

Observe that, in general, electrodes such as **21** and **22** are each respectively so functionally associated with a crystal wafer **10** that the direction of electric field propagation is along the axis **12**. The axis **12** is related to the crystallographic C-axis thru the angle theta. It is preferred to separate electrodes by a distance measured through the crystal by a distance greater than about 1 millimicron.

Referring once again to FIGURE 3, the plot there shown represents the generalized relationship between percent efficiency and theta in crystals of the invention. In a given crystal wafer an exact statement of the relationship between theta and percent efficiency is not practical because in a given crystal wafer, such as crystal wafer **10** in this description, normal manufacturing variables inherently operate to induce variances in the product crystal. These manufacturing variances typically cause the resulting properties of a length extensional

mode generated in a given crystal of this invention to vary slightly from a desired or even optimum condition.

It will be appreciated that the plot shown in FIGURE 3 is based upon the use of an optimum or preferred shape for a crystal of the invention, as described above and as illustrated in FIGURE 2. The plot of FIGURE 3 shows the entire AM series. For reasons similar to those just mentioned in reference to FIGURE 3, minor variations in any actual efficiency curve for a particular crystal of the invention tend to occur.

Surprisingly and unexpectedly, a crystal of this invention of the AM series displays greater electromechanical coupling efficiencies than is obtained by generating an acoustic length extensional mode along the crystallographic C-axis.

FIGURE 5 is a schematic view of a mechanical resonator constructed according to the teachings of W. P. Mason in his book "Electro-Mechanical Transducer and Wave Filters" (published by D. Van Nostrand Company, Inc., second èdition). Metallic electrodes **31** and **32** are adhered to the resonator body **30** which comprises an AM series zinc oxide single crystal prepared according to the teachings of this invention. Electrode **31** is connected to an appropriate signal source **34** and electrode **35** is connected to an appropriate receiver **35**. The resulting mechanical resonator has unexpectedly superior bandwidth of transmission when compared to a similar resonator constructed so as to utilize a conventional zinc oxide single crystal adapted to transduce acoustic length extensional waves on the crystallographic *c*-axis thereof.

FIGURE 6 is a schematic view of a quarter wave transducer constructed according to the teachings of W. P. Mason in his book "Electro-Mechanical Transducers and Wave Filters" (published by D. Van Nostrand Company, Inc., second edition). Metallic electrodes **61** and **62** are adhered to the resonator body **60** of zinc oxide AM series. The electrodes are connected to an appropriate signal source/receiver **64**. The resonator body **60** is adhered to the rigid support **63**. The resonator body is coupled to the piston-like motion **65** of the crystal by suitable means, such as oil, elastomer, or the like. Such transducers are used for ultrasonic underwater sound echo ranging and communications. The resulting mechanical resonator has unexpectedly superior bandwidth of transmission when compared to a similar device made using a single crystal zinc oxide with orientation on the crystallographic *c*-axis.

The following examples of particular embodiments are provided to further describe the invention. Each example employs at least one AM series zinc oxide crystal prepared as described above in reference to FIGURE 2. Using these examples devices may be constructed so as to operate on any part of the specified curves in FIGURE 3.

EXAMPLE I

The construction here is identical to that shown in FIGURE 5 and above described.

An AM single crystal zinc oxide wafer, having a resistivity of approximately 10^8 ohm-cm., is cut with a 1 mm. width, 5 mm. length, and a 0.05 mm. thickness along the AM series with theta equal to 61°. The wafer is electroded with sputtered indium overcoated with vapor deposited gold and has its opposed ends polished flat and perpendicular to the center line thereof. This wafer is mounted for resonance, antiresonance bandwidth measurement on a Q-meter. The bandwidth between the resonant frequency and anti-resonant frequency is one measure of the maximum bandwidth in a crystal filter. Similar measurements are made using a single crystal zinc oxide cut along the crystallographic *a*-axis. The bandwidth realized for the AM series crystal is approximately 2.6 times that obtained for the crystallographic *c*-axis crystal.

EXAMPLE II

The construction here is identical to that shown schematically in FIGURE 6 and above described.

An AM single crystal zinc oxide wafer, having a resistivity of approximately 10^8 ohm-cm., is cut with a width of 2 mm., length of 10 mm. and a thickness of 1.0 mm. in the AM series; theta equals 59°. The wafer is polished and electroded as described in Example I. The wafer is adhered to the mounting or supporting medium with a high strength epoxy. Near the resonant frequency (about 470 kilohertz) there is produced a piston-like to-and-fro motion at the nonmounted (free) end of the bar. The bandwidth of this quarter wavelength transduced is 26% which is nearly 1.6 times the value obtained for a similar construction using a conventional zinc oxide crystal cut to transducer along the crystallographic *c*-axis.

It will be obvious to those skilled in the art that the high length extensional electromechanical coupling coefficient of the AM series crystals has many device applications. The devices illustrated in the figures are to be considered illustrative and to be uunderstood as indicating the necessary transmission structures as are well known in the art for the transmission of electromagnetic signals. The foregoing examples are offered as exemplary of the magnitude of possible device designs which depend upon the basic teaching of this invention and are not to be construed as limiting the invention. Various other modifications and embodiments will become apparent to those skilled in the art. However, all such devices, which are characterized in whole or part by the basic phenomenon of the AM series through which this invention had advanced the art are properly considered within the spirit and scope of this invention.

I claim:

1. A piezoelectric device comprising at least one element consisting essentially of a piezoelectric zinc oxide crystal having Wurtzite crystal structure and characterized by being capable of propagating an acoustic length extensional mode with an efficiency greater than that obtained by generating such wave along the crystallographic *c*-axis, in response to a dynamic electric field applied across said crystal in the direction of acoustic length extensional mode generation, said crystal having both

(a) a resistivity between about 0.1 and 10^{12} ohm-cm., and

(b) an axis passing through the crystallographic *c*-axis and inclined at an angle theta relative to such crystallographic *c*-axis, theta ranging from about 42° to 78° and means for making electrode contact with said element on at least one face.

2. The piezoelectric device of claim **1** wherein said crystal is further characterized by having maximum length extensional mode coupling efficiency, said crystal further having a value of theta ranging from about 55° to 67°.

3. The piezoelectric device of claim **2** wherein theta is about 60°.

4. The piezoelectric device of claim **2** in which the smallest dimension of said element corresponds with the inclined axis at an angle theta relative to said crystallographic *c*-axis and in which electrode contact is made on two face perpendicular to said inclined axis.

5. An electromechanical resonator device comprising

(a) a piezoelectric device of claim **4**, and

(b) means for sending or receiving the resulting electrical signal generated near the mechanical resonant frequency.

6. An electromechanical transducer device comprising

(a) a piezoelectric device of claim **4**,

(b) means for sending the electrical signal, and

(c) means for receiving the mechanical signal.

7. An electromechanical transducer device comprising

(a) a piezoelectric device of claim **4**,

(b) means for sending the mechanical signal, and

(c) means for receiving the electrical signal.

References Cited

UNITED STATES PATENTS

2,204,762	6/1940	Mason	310—9.5
2,472,691	6/1949	Bond	310—9.5
2,975,354	3/1961	Rosen	310—8.1
3,091,707	5/1963	Hutson	310—8.1
3,122,662	2/1964	Mason	310—9.5
3,219,850	11/1965	Langevin	310—8.6
3,414,779	12/1968	Bohm	310—8.1
3,388,002	6/1968	Foster	117—217
3,397,328	8/1968	Schafft	310—8.1

FOREIGN PATENTS

104,047	6/1936	Australia.
366,642	1939	Italy.
355,429	9/1936	Italy.

J. D. MILLER, Primary Examiner

U.S. Cl. X.R.

310—805, 807