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# (54) Title: THIN FILM PIEZOELECTRIC DEVICE, PIEZOELECTRIC ACTUATOR, PIEZOELECTRIC SENSOR, HARD DISK DRIVE AND INK JET PRINTER DEVICE

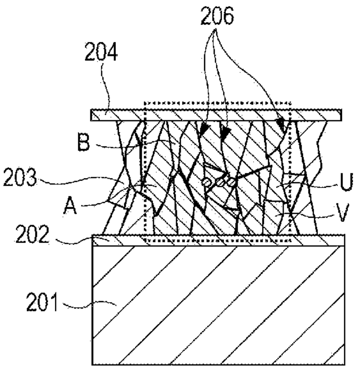


FIG. 3A

(57) **Abstract**: A thin film piezoelectric device according to the present invention includes a potassium sodium niobate-based piezoelectric thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less, and a pair of electrode films configured to hold the piezoelectric thin film therebetween.

WO 2014/045121 A1

## Title of Invention

THIN FILM PIEZOELECTRIC DEVICE, PIEZOELECTRIC ACTUATOR, PIEZOELECTRIC SENSOR, HARD DISK DRIVE AND INK JET PRINTER DEVICE

## Background of Invention

### Technical Field

[0001]

The present invention relates to a thin film piezoelectric device using a thin film piezoelectric material; a piezoelectric actuator and a piezoelectric sensor that include the thin film piezoelectric devices; and a hard disk drive and an ink jet printer device that include the piezoelectric actuators.

### Background Art

[0002]

When piezoelectric thin films are formed, crystallinity of films is controlled for achieving good piezoelectric characteristics. In order to realize high crystallinity, piezoelectric thin films are generally epitaxially grown on a single crystal substrate.

[0003]

General methods for producing piezoelectric thin films include dry methods such as an ion plating method, a sputtering method, an electron beam evaporation method, and an MOCVD method (metal-organic chemical vapor deposition method), and wet methods such as a sol-gel method and an MOD method (metal-organic decomposition method).

[0004]

Patent Literature 1 discloses an underlayer of a piezoelectric thin film, the underlayer being formed by a sputtering method. The c-axis orientation of the piezoelectric thin film is enhanced by using the underlayer having a smaller a-axis lattice constant than that of the piezoelectric thin film, resulting in enhancement of the piezoelectric characteristics of the piezoelectric thin film.

[0005]

Patent Literature 2 discloses an alkali niobate-based piezoelectric thin film composed of crystal grains the majority of which have a columnar structure having a longer length in the thickness direction than that in the planar direction of a substrate and which have an average crystal grain diameter of 0.1 μm or more and 1 μm or less in the planar direction of the substrate in order to realize a high piezoelectric constant.

[0006]

Patent Literature 3 discloses that a dielectric thin film is formed by an MOCVD method and then annealed in an atmosphere of oxidizing gas containing ozone to decrease defects in a network structure of the dielectric thin film, and consequently, a leakage current is decreased.

[Patent Literature]

[0007]

[PTL 1] Japanese Unexamined Patent Application Publication No. 11-026296

[PTL 2] Japanese Unexamined Patent Application Publication No. 2008-159807

[PTL 3] Japanese Unexamined Patent Application Publication No. 10-182300

## Summary of Invention

[0008]

As described above, in order to realize practical piezoelectric characteristics of an alkali niobate-based piezoelectric thin film, the average crystal grain diameter is required to be controlled in a proper range.

[0009]

However, with a larger crystal grain diameter, when oxygen deficiencies occur in grain boundaries formed in the thickness direction (perpendicular to an electrode film), the grain boundaries serve as current paths, increasing the risk of increasing a leakage current between electrode films. Fig. 2A is a schematic view illustrating a section of an alkali niobate-based piezoelectric thin film in which a leakage current is increased by an average crystal grain diameter larger than a proper range, and Fig. 2B illustrates an actually observed image.

A thin film piezoelectric device shown in Figs. 2A and 2B includes a substrate 101, a lower electrode 102, piezoelectric thin film 103 and upper electrode 104, and grains of the piezoelectric thin film 103 are separated by grain boundaries 106.

[0010]

This problem is a matter of great concern for manufacture of a thin film piezoelectric device and reliability thereof. As described above, a generally used countermeasure is to anneal a piezoelectric thin film after deposition thereof, but even when a dielectric thin film is formed by the sputtering method and then annealed, some extent of effect is obtained, but it is difficult to eliminate oxygen deficiencies in all grain boundaries in the film. Therefore, annealing after film formation is not a satisfactory countermeasure for decreasing a leakage current between electrode films.

[0011]

The present invention has been achieved in consideration of the problem and is aimed at making it possible to enhance the reliability of a thin film piezoelectric device by decreasing a leakage current between electrode films without deterioration in piezoelectric characteristics of a potassium sodium niobate-based piezoelectric thin film (hereinafter referred to as a "KNN thin film").

[0012]

A thin film piezoelectric device according to the present invention includes a potassium sodium niobate-based piezoelectric thin film (KNN thin film) which has an average crystal grain diameter of 60 nm or more 90 nm or less, and a pair of electrode layers configured to hold the piezoelectric thin film therebetween. When the KNN thin film formed by crystal growth has an average crystal grain diameter within this range, a leakage current between electrode films formed on and below the piezoelectric thin film in the thin film piezoelectric device can be decreased. The potassium sodium niobate-based piezoelectric thin film refers to a thin film having a composition represented by the basic chemical formula $(Na_xK_{1-x})NbO_3$ $(0 < x 1)$ and, if required, containing various additives at the A site where an alkali metal is present and the B site where Nb is present.

[0013]

Here, the average crystal grain diameter according to the present invention is defined. Specifically, the average crystal grain diameter is calculated by image analysis of an image obtained by observing a surface of the piezoelectric thin film with a scanning electron microscope (hereinafter referred to as "SEM") within a field of view at an image magnification of 5000 times. The diameter of each crystal grain is determined by approximating the shape as a circular shape. The average of the approximate crystal grain diameters is considered as the average crystal grain diameter (refer to Fig. 4).

[0014]

Further, the piezoelectric thin film according to the present invention preferably has a structure in which a section in a direction perpendicular to the electrode films contains a portion where a plurality of grains are present in the thickness direction of the piezoelectric thin film, and a ratio of total sectional area of the grains constituting the portion where the plurality of grains are present is 50% or more of the whole sectional area of the piezoelectric thin film.

[0015]

Here, the section is a surface obtained by cutting, with a machine or focused ion beam (hereinafter referred to as "FIB"), a laminate including the piezoelectric thin film in the thickness direction of the piezoelectric thin film, and a broken-out surface thereof is observed with SEM or a transmission electron microscope (hereinafter referred to as "TEM") at an image magnification of 10000 times. The expression "a portion where a plurality of grains are present in the thickness direction of the piezoelectric thin film" represents a portion where at least two particles are deposited in the thickness direction as shown in Figs. 3A and 3B. In addition, "the total sectional area of the grains constituting the portion where a plurality of grains are present" represents a total of sectional areas of grains A to V shown in Fig. 3A or sectional areas of grains A to I shown in Fig. 3B. Fig. 3C shows an actual TEM image.

A thin film piezoelectric device according to the present invention shown in Figs. 3A to 3C includes a substrate 201, a lower electrode 202, piezoelectric thin film 203 and upper electrode 204, and grains of the piezoelectric thin film 203 are separated by grain boundaries 206.

[0016]

The piezoelectric thin film of the present invention preferably contains Mn (manganese). When the thin film contains Mn, a leakage current can be decreased, and high piezoelectric characteristic -d31 can be achieved.

[0017]

In addition, the piezoelectric thin film of the present invention preferably contains at least three elements of Li (lithium), Sr (strontium), Ba (barium), Zr (zirconium), and Ta (tantalum). When the thin film contains these elements, a leakage current can be decreased, and high piezoelectric characteristic -d31 can be achieved.

[0018]

According to the present invention, the average crystal grain diameter of crystal grains which constitute a potassium sodium niobate-based piezoelectric thin film is adjusted in a predetermined range, and thus both the two important characteristics for a thin film piezoelectric device, i.e., improved piezoelectric characteristics and decreased leakage current between electrode films, can be satisfied.

A piezoelectric actuator according to the present invention includes the thin film piezoelectric device with increased piezoelectric properties and reduced leakage current and can improve the deformation characteristics, and a piezoelectric sensor according to the present invention includes the thin film piezoelectric device with increased piezoelectric properties and reduced leakage current and can improve the detecting sensitivity. Therefore, a high performance hard disk drive and ink jet printer device can be provided.

## Brief Description of Drawings

[0019]

[Fig. 1] Fig. 1 is a drawing of a configuration of a thin film piezoelectric device according to the present invention.

[Fig. 2A] Fig. 2A is a schematic drawing of a sectional structure of a piezoelectric thin film having high crystallinity.

[Fig. 2B] Fig. 2B is an image of a transmission electron microscope (TEM) of the sectional structure.

[Figs. 3A and 3B] Figs. 3A and 3B are each a schematic drawing of a sectional structure of a potassium sodium niobate-based piezoelectric thin film according to the present invention.

[Fig. 3C] Fig. 3C is an image of a transmission electron microscope (TEM) of the sectional structure.

[Fig. 4] Fig. 4 is a drawing illustrating the definition of an average crystal grain diameter according to the present invention.

[Figs. 5A to 5B] Figs. 5A and 5B are structural diagrams of piezoelectric actuators according to the present invention.

[Figs. 6A to 6D] Figs. 6A to 6D are structural diagrams of piezoelectric sensors according to the present invention.

[Fig. 7] Fig. 7 is a structural diagram of a hard disc drive according to the present invention.

[Fig. 8] Fig. 8 is a structural diagram of an ink jet printer device according to the present invention.

## Description of Embodiments

[0020]

A preferred embodiment of the present invention is described in detail below with reference to the drawings.

[0021]

Fig. 1 illustrates a configuration of a thin film piezoelectric device 10 according to an embodiment of the present invention.

[0022]

A substrate 1 is composed of single crystal silicon, sapphire, magnesium oxide, or the like, and single crystal silicon is particularly preferred from the viewpoint of cost and handleability in a process. The thickness of the substrate 1 is generally 10 to 1000 μm.

[0023]

A lower electrode film 2 is formed on the substrate 1. As a material, Pt (platinum) and Rh (rhodium) are preferred. The forming method is a vapor deposition method or a sputtering method. The thickness is preferably 50 to 1000 nm.

[0024]

A piezoelectric thin film 3 is formed on the lower electrode film 2. The piezoelectric thin film 3 is a potassium sodium niobate-based piezoelectric thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less.

[0025]

With an average crystal grain diameter of less than 60 nm, the piezoelectric characteristic -d31 is decreased to be lower than a value satisfactory for practical use of a thin film piezoelectric device, while with an average crystal grain diameter exceeding 90 nm, a leakage current between electrode films is increased to be higher than an upper limit for practical use of a thin film piezoelectric device. A smaller average crystal grain diameter enables deposition of a plurality of crystal grains in the thickness of the piezoelectric thin film 3. This is schematically shown in Figs. 3A and 3B, in which grain boundaries of grains are complicated between electrode films, increasing the total length of the grain boundaries between the electrode films.

[0026]

A section of the piezoelectric thin film 3 in a direction perpendicular to the electrode films contains a portion where a plurality of grains are present in the thickness direction of the piezoelectric thin film 3, and a ratio of total sectional area of the grains constituting the portion where the plurality of grains are present is preferably 50% or more, more preferably 70% or more, of a total sectional area of the piezoelectric thin film 3. When the ratio of total sectional area of the portion where the plurality of grains are present in the thickness direction of the piezoelectric thin film 3 to the total sectional area of the film is within the above-described range, grain boundaries between the electrode films are complicated to increase the length of the grain boundaries, thereby decreasing a leakage current between the electrode films.

[0027]

The piezoelectric thin film 3 preferably contains Mn (manganese). In this case, the leakage current of the thin film piezoelectric device 10 can be decreased, and higher piezoelectric characteristic -d31 can be achieved.

A technology to improve a leakage current characteristic by reducing the hole density and oxygen vacancies through addition of Mn (manganese) to a KNN thin film is known.

[0028]

The piezoelectric thin film 3 preferably contains at least three elements of Li (lithium), Sr (strontium), Ba (barium), Zr (zirconium), and Ta (tantalum). When the thin film 3 contains these elements, the leakage current can be decreased, and higher piezoelectric characteristic -d31 can be achieved.

The piezoelectric thin film 3 includes K(potassium) and Na(sodium) which are easy to evaporate in deposition processes as main components, and the addition of above elements stabilizes the composition of alkali metals in the piezoelectric thin film. So, we can obtain the composition of the piezoelectric thin film on-target.

Moreover, addition of the above elements tends not to cause a depolarization in piezoelectric thin film in processes under high temperature, and the reliability of the thin film piezoelectric device can be improved.

[0029]

The thickness of the piezoelectric thin film 3 is not particularly limited and, for example, can be about 0.5 $\mu$m to 10 $\mu$m.

[0030]

Next, an upper electrode film 4 is formed on the piezoelectric thin film 3. The material is preferably Pt or Rh which is the same as the lower electrode film 2. The thickness is preferably 50 nm to 1000 nm.

[0031]

Then, a laminate including the piezoelectric thin film 3 is patterned by photolithography and dry etching or wet etching, and finally the substrate 1 is cut to produce the thin film piezoelectric device 10. The substrate 1 may be removed from the thin film piezoelectric device 10, producing a thin film piezoelectric thin film including only the laminate. In addition, after the laminate is patterned, a protective film may be formed using polyimide or the like.

[0032]

A method for evaluating the piezoelectric thin film 3 according to the embodiment of the present invention is as follows.

(1) Calculation of average crystal grain diameter:

A surface of the piezoelectric thin film 3 after formation is observed with a scanning electron microscope (hereinafter referred to as "SEM") within a field of view at an image magnification of 5000 times, followed by image analysis of the resultant image. The diameter of each crystal grain is determined by approximating the shape as a circular shape. The average of the approximate crystal grain diameters is considered as the average crystal grain diameter (refer to Fig. 4).

(2) Calculation of ratio of area in which a plurality of grains are present in the thickness direction of the piezoelectric thin film 3:

After the upper electrode film 4 is formed on the piezoelectric thin film 3, the piezoelectric thin film 3 is cut in the thickness direction of the piezoelectric thin film 3 with a machine or focused ion beam (hereinafter referred to as "FIB"), and a cut surface is observed with SEM or a transmission electron microscope (hereinafter referred to as "TEM") at an image magnification of 10000 times. The total sectional area of crystal grains in the portion where the plurality of grains are present in the thickness direction of the piezoelectric thin film 3 is determined, and the total sectional area is divided by the total area of the section within the observation range (refer to Figs. 3A and 3B).

(3) Measurement of leakage current density between electrode films:

The substrate 1 is cut into a size of 5 mm × 20 mm to produce the thin film piezoelectric device 10, which is then measured by applying DC ±20 V between the upper and lower electrode films 2 and 4 thereof. A ferroelectric evaluation system TF-1000 (manufactured by aixACCT Corporation) is used as an evaluation apparatus. The voltage application time is 2 seconds.

(4) Measurement of piezoelectric constant -d31:

Voltages of 3 $V_{p-p}$ and 20 $V_{p-p}$ at 700 Hz are applied between the upper and lower electrode films 2 and 4 of the thin film piezoelectric device 10, and a displacement at the tip of the thin film piezoelectric device 10 is measured with a laser Doppler vibrometer and an oscilloscope.

The piezoelectric constant -d31 can be determined by calculation according to the following expression (1):

$$d_{31} \cong -\frac{h_s^2}{3L^2}\frac{s_{11,p}}{s_{11,s}}\frac{\delta}{V}$$ Expression (1)

$h_s$: thickness of Si substrate [400 μm], $S_{11,p}$: elastic compliance of KNN thin film [1/104 GPa], $S_{11,s}$: elastic compliance of Si substrate [1/168 GPa], L: length of drive portion [13.5 mm], δ: displacement, V: applied voltage

(Embodiment 1)

[0033]

A lower electrode film 2 is formed by crystal growth on a substrate 1 composed of single crystal silicon to form an underlayer of a piezoelectric thin film 3 (KNN thin film). The lower electrode film 2 is a Pt film and has a thickness of 50 to 1000 nm. The formation method is a sputtering method, and the film is formed under heating of the substrate 1 at 500℃.

[0034]

Then, the piezoelectric thin film 3 (KNN thin film) is formed using a (K, Na)$NbO_3$ sputtering target. The formation method is a sputtering method, and like the lower electrode film 2, the piezoelectric thin film 3 is formed under a condition where the substrate 1 is at a high temperature.

[0035]

The substrate temperature is set to 520°C to 460°C. Ata substrate temperature of 520°C or less, crystal growth is inhibited, resulting in a decrease in average crystal grain diameter of the piezoelectric thin film 3. At a set temperature of 460°C or more, the average crystal grain diameter of the piezoelectric thin film 3 can be prevented from being excessively decreased, and deterioration in the piezoelectric constant -d31 can be prevented.

[0036]

As noted above, smaller average crystal grain diameter enables deposition of a plurality of crystal grains in the thickness of the piezoelectric thin film 3. This is schematically shown in Figs. 3A and 3B, in which grain boundaries of grains are complicated between electrode films, increasing the total length of the grain boundaries between the electrode films.

[0037]

The inventors of the present invention suppose the following formation mechanism of a leakage path. A main cause for the leakage path lies in oxygen deficiencies in grain boundaries. The oxygen deficiencies are partially produced by causes, such as heat history, an oxygen partial pressure during film deposition, film thickness, amounts of additives, etc., not uniformly distributed in all grain boundaries. As the total length of grain boundaries increases, the ratio of positions where oxygen deficiencies are present to the total length of grain boundaries decreases, resulting in a decrease in leakage path. Assuming that the incidence rate of a leakage path due to one grain boundary is A%, and the number of crystal grains deposited in the thickness direction is N, the risk of causing a continuous leakage path by the crystal grains is $A_N$%. On the other hand, as shown in Fig. 2A, with higher crystallinity, the number of crystal grains deposited between the electrode films is 1, and thus the risk of causing a leakage path due to grain boundaries is A%. Because it is essential that $A > A^N$, deposition of a plurality of crystal grains in the thickness direction has the effect of decreasing a leakage current between the electrode films.

[0038]

However, as described above, the piezoelectric characteristic -d31 is decreased by excessively decreasing the average crystal grain diameter. Therefore, it is necessary to realize a decrease in leakage current while maintaining piezoelectric characteristics required for the thin film piezoelectric device 10 by controlling the average crystal grain diameter in an appropriate range.

[0039]

Next, the average crystal grain diameter in a surface of the piezoelectric thin film 3 (KNN thin film) is measured by the above-described method.

[0040]

Then, an upper electrode film 4 is formed on the piezoelectric thin film 3 by the sputtering method. Like the lower electrode film 2, the material is preferably a Pt film. The thickness is 50 to 1000 nm.

[0041]

Next, a laminate including the piezoelectric thin film 3 is patterned by photolithography and dry etching or wet etching, and finally the substrate 1 is cut into a size of 5 mm × 20 mm, producing a plurality of thin film piezoelectric devices 10.

[0042]

One of the resultant thin film piezoelectric devices 10 is cut, and a ratio of an area where a plurality of grains is present in a section is determined by the above-described method. In addition, the leakage current density between the electrode films and piezoelectric constant -d31 are measured using another one of the thin film piezoelectric devices 10. From a practical viewpoint, the thin film piezoelectric device 10 is required to have a leakage current density of $1 \times 10^{-6}$ A/cm$^2$ or less, and -d31 of 70 pm/V or more.

(Embodiment 2)

[0043]

A sputtering target containing (K, Na)$NbO_3$ and Mn added as an additive in a range of 0.1 to 3.0 atomic % is used instead of the (K, Na)$NbO_3$ sputtering target used in Embodiment 1. A Mn adding amount of 3.0 atomic % or less tends to suppress a decrease in -d31 of the piezoelectric thin film 3 (KNN thin film), and a Mn adding amount of 0.1 atomic % or more tends to easily achieve the effect of decreasing the leakage current between the electrode films.

[0044]

The substrate temperature is set to 520°C to 480°C. Ata substrate temperature of 520°C or less, crystal growth is inhibited, resulting in a decrease in average crystal grain diameter of the piezoelectric thin film 3. At a set temperature of 480°C or more, the average crystal grain diameter of the piezoelectric thin film 3 can be prevented from being excessively decreased, and deterioration in the piezoelectric constant -d31 can be prevented. The conditions other than the sputtering target and the substrate set temperature are the same as in Embodiment 1.

(Embodiment 3)

[0045]

A sputtering target further containing at least three additives selected from Li, Sr, Ba, Zr, Ta and added as additives is used instead of the sputtering target (K, Na)$NbO_3$ used in Embodiment 1. The ranges of amounts of the elements added are Li: 0.1 to 3.0 atomic %, Sr: 0.5 to 6.0 atomic %, Ba: 0.05 to 0.3 atomic %, Zr: 0.5 to 6.0 atomic %, and Ta: 0.01 to 15 atomic %. By setting the upper limit of the amount of each of the elements added to the above-described value, deterioration in the piezoelectric constant -d31 tends to be prevented. By setting the lower limit of the amount of each of the elements added to the above-described value, the piezoelectric constant -d31 tends to be improved. Additionally, Mn may be added in the same range as in Embodiment 2.

[0046]

The substrate temperature is set to 520°C to 470°C. At a substrate temperature of 520°C or less, crystal growth is inhibited, resulting in a decrease in average crystal grain diameter of the piezoelectric thin film 3 (KNN thin film). At a set temperature of 470°C or more, the average crystal grain diameter of the piezoelectric thin film 3 can be prevented from being excessively decreased, and deterioration in the piezoelectric constant -d31 can be prevented. The conditions other than the sputtering target and the substrate set temperature are the same as in Embodiment 1.

[0047] (Piezoelectric actuator)

Fig. 5A is a structural diagram of a head assembly mounted on a hard disk drive as an example of piezoelectric actuators including these piezoelectric elements. As shown in this drawing, a head assembly 200 includes a base plate 9, a load beam 11, a flexure 17, first and second piezoelectric elements 13 serving as driver elements, and a slider 19 provided with a head element 19a, as main constituents thereof.

[0048]

In this regard, the load beam 11 includes a base end portion 11b fixed to the base plate 9 by beam welding or the like, first and second plate spring portions 11c and 11d extending from this base end portion 11b while tapering, an opening portion 11e disposed between the first and second plate spring portions 11c and 11d, and a beam main portion 11f following the first and second plate spring portions 11c and 11d and extending linearly while tapering.

[0049]

The first and second piezoelectric elements 13 are disposed on a wiring flexible substrate 15 which is part of the flexure 17, while keeping a predetermined distance from each other. The slider 19 is fixed to an end portion of the flexure 17 and is rotated in accordance with expansion and contraction of the first and second piezoelectric elements 13.

[0050]

The first and second piezoelectric elements 13 are formed from a first electrode layer, a second electrode layer, and a piezoelectric layer sandwiched between the first and second electrode layers. High voltage resistance and a sufficient displacement can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as this piezoelectric layer.

[0051]

Fig. 5B is a configuration diagram of a piezoelectric actuator of an ink-jet printer head, as another example of the piezoelectric actuator including the above-described piezoelectric element.

[0052]

A piezoelectric actuator 300 is formed by stacking an insulating layer 23, a lower electrode layer 24, a piezoelectric layer 25, and an upper electrode layer 26 on a substrate 20.

[0053]

In the case where a predetermined discharge signal is not supplied and a voltage is not applied between the lower electrode layer 24 and the upper electrode layer 26, deformation does not occur in the piezoelectric layer 25. A pressure change does not occur in a pressure chamber 21 provided with a piezoelectric element supplied with no discharge signal, and an ink droplet is not discharged from a nozzle 27 thereof.

[0054]

On the other hand, in the case where a predetermined discharge signal is supplied and a certain voltage is applied between the lower electrode layer 24 and the upper electrode layer 26, deformation occurs in the piezoelectric layer 25. The insulating film 23 is bent to a great extent in a pressure chamber 21 provided with the piezoelectric element supplied with a discharge signal. Consequently, the pressure in the pressure chamber 21 increases instantaneously, and an ink droplet is discharged from the nozzle 27.

[0055]

Here, high voltage resistance and a sufficient displacement can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as the piezoelectric layer.

[0056] (Piezoelectric sensor)

Fig. 6A is a structural diagram (plan view) of a gyro sensor as an example of a piezoelectric sensor including the above-described piezoelectric element. Fig. 6B is a sectional view of the section taken along a line A-A shown in Fig. 6A.

[0057]

A gyro sensor 400 is a tuning folk vibrator type angular velocity detecting element provided with a base portion 110 and two arms 120 and 130 connected to one surface of the base portion 110. This gyro sensor 400 is obtained by micromachining the piezoelectric layer 30, the upper electrode layer 31, and the lower electrode layer 32 constituting the above-described piezoelectric element to correspond with the shape of the tuning folk vibrator. The individual portions (base portion 110 and arms 120 and 130) are integrally formed by the piezoelectric element.

[0058]

Each of drive electrode layers 31a and 31b and detection electrode layer 31d is disposed on a first principal surface of one arm 120. Likewise, each of drive electrode layers 31a and 31b and detection electrode layer 31c is disposed on a first principal surface of the other arm 130. Each of these electrode layers 31a, 31b, 31c, and 31d is obtained by etching the upper electrode layer 31 into a predetermined electrode shape.

[0059]

Meanwhile, the lower electrode layer 32 disposed all over second principal surfaces (principal surface on the back side of the first principal surface) of the base portion 110 and the arms 120 and 130 functions as a ground electrode of the gyro sensor 400.

[0060]

Here, the longitudinal direction of each of the arms 120 and 130 is specified to be a Z direction, and a plane including the principal surfaces of the two arms 120 and 130 is specified to be an XZ plane, so that an XYZ rectangular coordinate system is defined.

[0061]

When a drive signal is supplied to the drive electrode layers 31a and 31b, the two arms 120 and 130 are excited in an in-plane vibration mode. The in-plane vibration mode refers to a vibration mode in which the two arms 120 and 130 are excited in a direction parallel to the principal surfaces of the two arms 120 and 130. For example, when one arm 120 is excited in a -X direction at a velocity V1, the other arm 130 is excited in a +X direction at a velocity V2.

[0062]

In the case where rotation at an angular velocity ω is added to the gyro sensor 400 under this state while the axis of rotation is specified to be the Z axis, the Coriolis force is applied to each of the two arms 120 and 130 in a direction orthogonal to the direction of the velocity, and excitation occurs in an out-of-plane vibration mode. The out-of-plane vibration mode refers to a vibration mode in which the two arms 120 and 130 are excited in a direction orthogonal to the principal surfaces of the two arms 120 and 130. For example, when the Coriolis force F1 applied to one arm 120 is in a -Y direction, a Coriolis force F2 applied to the other arm 130 is in a +Y direction.

[0063]

The magnitudes of the Coriolis forces F1 and F2 are proportionate to the angular velocity ω and, therefore, the angular velocity ω can be determined by converting mechanical strains of the arms 120 and 130 due to the Coriolis forces F1 and F2 to electric signals (detection signals) by the piezoelectric layer 30 and taking them from the detection electrode layers 31c and 31d.

[0064]

High voltage resistance and sufficient detection sensitivity can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as this piezoelectric layer.

[0065]

Fig. 6C is a configuration diagram of a pressure sensor as a second example of the piezoelectric sensor including the above-described piezoelectric element.

[0066]

A pressure sensor 500 has a cavity 45 to respond to application of a pressure and, in addition, is formed from a support member 44 to support a piezoelectric element 40, a current amplifier 46, and a voltage measuring instrument 47. The piezoelectric element 40 includes a common electrode layer 41, a piezoelectric layer 42, and an individual electrode layer 43, which are stacked in that order on the support member 44. Here, when an external force is applied, the piezoelectric element 40 is bent and the voltage is detected by the voltage measuring instrument 47.

[0067]

High voltage resistance and sufficient detection sensitivity can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as this piezoelectric layer. [0068]

Fig. 6D is a configuration diagram of a pulse wave sensor as a third example of the piezoelectric sensor including the above-described piezoelectric element.

[0069]

A pulse wave sensor 600 is configured to be equipped with a transmitting piezoelectric element and a receiving piezoelectric element on a substrate 51. Here, in the transmitting piezoelectric element, electrode layers 54a and 55a are disposed on the two surfaces of the transmitting piezoelectric layer 52 in the thickness direction, and in the receiving piezoelectric element, electrode layers 54b and 55b are also disposed on the two surfaces of the receiving piezoelectric layer 53 in the thickness direction. In addition, electrodes 56 and upper surface electrodes 57 are disposed on the substrate 51, where the electrode layers

54b and 55b are electrically connected to the upper surface electrodes 57, respectively, by wirings.

[0070]

In order to detect pulses of a living body, initially, the substrate back surface (surface not equipped with the piezoelectric element) of the pulse wave sensor 600 is brought into contact with the living body. Then, when pulses are detected, a specific drive voltage signal is output to both the electrode layers 54a and 55a of the transmitting piezoelectric element. The transmitting piezoelectric element is excited in accordance with the drive voltage signal input into both the electrode layers 54a and 55a, so as to generate an ultrasonic wave and transmit the ultrasonic wave into the living body. The ultrasonic wave transmitted into the living body is reflected by a bloodstream and is received by the receiving piezoelectric element. The receiving piezoelectric element converts the received ultrasonic wave to a voltage signal and outputs from both the electrode layers 54b and 55b.

[0071]

High voltage resistance and sufficient detection sensitivity can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as both the piezoelectric layers.

[0072] (Hard disk drive)

Fig. 7 is a configuration diagram of a hard disk drive equipped with the head assembly shown in Fig. 5A.

[0073]

A hard disk drive 700 is provided with a hard disc 61 serving as a recording medium and a head stack assembly 62 to record the magnetic information thereto and regenerate in a cabinet 60. The hard disk 61 is rotated by a motor, although not shown in the drawing.

[0074]

In the head stack assembly 62, a plurality of assemblies formed from an actuator arm 64 supported by a voice coil motor 63 in such a way as to rotate freely around a spindle and a head assembly 65 connected to this actuator arm 64 are stacked in the depth direction in the drawing. The head slider 19 is attached to an end portion of the head assembly 65 in such a way as to opposite to the hard disk 61 (refer to Fig. 5A).

[0075]

As for the head assembly 65, a form in which the head element 19a (refer to Fig. 5A) is fluctuated in two steps is adopted. Relatively large movements of the head element 19a are controlled by whole drive of the head assembly 65 and the actuator arm 64 on the basis of the voice coil motor 63, and fine movements are controlled by drive of the head slider 19 by the end portion of the head assembly 65.

[0076]

High voltage resistance and sufficient accessibility can be obtained by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as the piezoelectric layer in this piezoelectric element used for this head assembly 65.

[0077] (Ink jet printer device)

Fig. 8 is a configuration diagram of an ink-jet printer device equipped with the ink-jet printer head shown in Fig. 5B.

[0078]

An ink-jet printer device 800 is configured to primarily include an ink-jet printer head 70, a main body 71, a tray 72, and a head drive mechanism 73.

[0079]

The ink-jet printer device 800 is provided with ink cartridges of four colors of yellow, magenta, cyan, and black in total and is configured to be able to perform full color printing. In addition, this ink-jet printer device 800 is provided with an exclusive controller board and the like in the inside, and the ink discharge timing of the ink-jet printer head 70 and scanning of the head drive mechanism 73 are controlled. Meanwhile, the main body 71 is provided with the tray 72 on the back and is provided with an automatic sheet feeder (automatic continuous sheet feeding mechanism) 76 in the inside, so as to automatically send recording paper 75 and deliver the recording paper 75 from a front-mounted delivery port 74.

[0080]

An ink-jet printer device having high voltage resistance and high safety can be provided by using the piezoelectric layer exhibiting a small leakage current and a large displacement, according to the present invention, as this piezoelectric layer in the piezoelectric element used for the piezoelectric actuator of this ink-jet printer head 70.

## Examples

[0081]

The present invention is described in further detail below based on examples and comparative examples, but the present invention is not limited to these examples.

(Example 1)

[0082]

A lower electrode film 2 was formed by crystal growth on a substrate 1 of single crystal Si to form an underlayer of a KNN thin film serving as a piezoelectric thin film 3. The lower electrode film 2 included a Pt film and had a thickness of 200 nm. The lower electrode film 2 was formed by the sputtering method under a condition in which the substrate was at 500°C.

[0083]

Then, the KNN thin film was deposited using a (K, Na)$NbO_3$ sputtering target. The KNN film was formed by the sputtering method under a condition in which the substrate was at 520°C. The thickness of the KNN film was 2.0 $\mu$m.

[0084]

In order to evaluate the average crystal grain diameter of the piezoelectric thin film 3, a surface of the piezoelectric thin film 3 was observed with SEM. A SEM image of the film surface was taken at an observation magnification of 5000 times, followed by image analysis. The diameter of each of the crystal grains was determined by approximating the shape as a circular shape. The average of the approximate diameters of the crystal grains was considered as the average crystal grain diameter. In this example, the average crystal grain diameter was 90 nm.

[0085]

Next, Pt was deposited to form an upper electrode film 4. The same sputtering method as for the lower electrode film 2 was used as a formation method, but the substrate temperature was 200°C. The thickness of the film was 200 nm.

[0086]

Next, a laminate including the piezoelectric thin film 3 was patterned by photolithography and dry etching or wet etching, and further the substrate was cut into a size of 5 mm × 20 mm, producing a plurality of thin film piezoelectric devices 10.

[0087]

The ratio of an area where a plurality of grains were present in the thickness direction of the piezoelectric thin film 3 was determined. In order to observe a section of the piezoelectric thin film 3, a portion of the thin film piezoelectric device 10 was cut in the thickness direction using FIB to form a cut surface. The cut surface was observed with TEM at an observation magnification of 10000 times to form a sectional image. Then, the total of areas of crystal grains in a portion where a plurality of grains were present in the thickness direction of the piezoelectric thin film 3 was determined and divided by the total area of the section within the observation range to calculate the ratio of an area where a plurality of grains were present in the thickness direction. The obtained ratio was 42%.

[0088]

In addition, the piezoelectric characteristic -d31 of another thin film piezoelectric device 10 was evaluated. Voltages of 3 $V_{p-p}$ and 20 $V_{p-p}$ at 700 Hz were applied between the upper and lower electrode films of the thin film piezoelectric device 10, and a displacement at the tip of the thin film piezoelectric device 10 was measured with a laser Doppler vibrometer and an oscilloscope.
The piezoelectric constant -d31 was determined by calculation according to the following expression (1):

$$d_{31} \cong -\frac{h_s^2}{3L^2}\frac{s_{11,p}}{s_{11,s}}\frac{\delta}{V}$$ Expression (1)

$h_s$: thickness of Si substrate [400 μm], $S_{11,p}$: elastic compliance of KNN thin film [1/104 GPa], $S_{11,s}$: elastic compliance of Si substrate [1/168 GPa], L: length of drive portion [13.5 mm], δ: displacement, V: applied voltage

The piezoelectric constant -d31 was 89 (pm/V) at 3 $V_{p-p}$ and 89 (pm/V) at 20 $V_{p-p}$.

[0089]

Table 1 shows the substrate temperature during deposition of the piezoelectric thin film 3, the film thickness, the average crystal grain diameter, the area ratio of deposited grains in the section to the total sectional area, the leakage current density, and the piezoelectric constant -d31 in Example 1.

(Examples 2 to 7 and Comparative Examples 1 to 3)

[0090]

A thin film piezoelectric device 10 was manufactured and evaluated with respect to the characteristics thereof in the same manner as in Example 1 except that the piezoelectric thin film 3 was formed at a substrate temperature shown in Table 1. The manufacture conditions and evaluation results are shown in Table 1.

(Examples 8 to 12 and Comparative Examples 4 and 5)

[0091]

A (K, Na)$NbO_3$ sputtering target containing 0.4 atomic % of Mn was used for forming the piezoelectric thin film 3, and the piezoelectric thin film 3 was formed at a substrate temperature shown in Table 1. Under the same other conditions as in Example 1, a thin film piezoelectric device 10 was manufactured, and the characteristics thereof were evaluated. The manufacture conditions and evaluation results are shown in Table 1.

(Examples 13 to 16 and Comparative Examples 6 and 7)

[0092]

A (K, Na)$NbO_3$ sputtering target containing 1.5 atomic % of Li, 0.1 atomic % of Ba, and 4 atomic % of Ta was used for forming the piezoelectric thin film 3, and the piezoelectric thin film 3 was formed at a substrate temperature shown in Table 1. Under the same other conditions as in Example 1, a thin film piezoelectric device 10 was manufactured, and the characteristics thereof were evaluated. The manufacture conditions and evaluation results are shown in Table 1.

(Examples 17 to 20 and Comparative Examples 8 and 9)

[0093]

A (K, Na)$NbO_3$ sputtering target containing 0.4 atomic % of Mn, 1.5 atomic % of Li, 0.1 atomic % of Ba, and 4 atomic % of Ta was used for forming the piezoelectric thin film 3, and the piezoelectric thin film 3 was formed at a substrate temperature shown in Table 1. Under the same other conditions as in Example 1, a thin film piezoelectric device 10 was manufactured, and the characteristics thereof were evaluated. The manufacture conditions and evaluation results are shown in Table 1.

(Examples 21 to 24 and Comparative Examples 10 and 11)

[0094]

A (K, Na)$NbO_3$ sputtering target containing 0.4 atomic % of Mn, 1.5 atomic % of Li, 3.0 atomic % of Sr, 0.1 atomic % of Ba, 3.0 atomic % of Zr, and 4 atomic % of Ta was used for forming the piezoelectric thin film 3, and the piezoelectric thin film 3 was formed at a substrate temperature shown in Table 1. Under the same other conditions as in Example 1, a thin film piezoelectric device 10 was manufactured, and the characteristics thereof were evaluated. The manufacture conditions and evaluation results are shown in Table 1.

[0095]

It was confirmed that the thin film piezoelectric devices 10 of Examples 1 to 24 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and the pair of electrode films formed to hold the KNN thin film therebetween have larger piezoelectric constants -d31 at 20 $V_{p-p}$ than in Comparative Examples 1 to 11 having an average crystal grain diameter out of the range. This is realized by providing the thin film piezoelectric devices 10 of Examples 1 to 24 with both the characteristic of a leakage current density of $1.0 \times 10^{-6}$ $A/cm^2$ or less, which is the minimum required for practical application, and the piezoelectric characteristics which can be secured by controlling the average crystal grain diameter to 60 nm or more and 90 nm or less. In Comparative Example 1 having a larger piezoelectric constant -d31 at 3 $V_{p-p}$, the piezoelectric constant -d31 at 20 $V_{p-p}$ is low because the piezoelectric constant -d31 cannot be normally measured at 20 $V_{p-p}$ due to a high leakage current density.

[0096]

It was also confirmed that the thin film piezoelectric devices 10 of Examples 2 to 24 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and having a deposited grain area ratio of 50% or more in the section exhibit lower leakage current densities than that of the thin film piezoelectric device 10 of Example 1 including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less but having a deposited grain area ratio of 50% or less in the section.

[0097]

Comparing the leakage current densities of the thin film piezoelectric devices 10 of Examples 8 to 12 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and containing Mn with the leakage current densities of the thin film piezoelectric devices 10 of Examples 1 to 7 each including the KNN thin film having substantially the same average crystal grain diameter (±5%) as in Examples 8 to 12 but not containing Mn, it was confirmed that the thin film piezoelectric devices 10 of Examples 8 to 12 have lower leakage current densities.

[0098]

It was further confirmed that the thin film piezoelectric devices 10 of Examples 13 to 16 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and containing three elements selected from Li, Ba, Ta, Sr, and Zr exhibit higher piezoelectric constants -d31 than those of the thin film piezoelectric devices 10 of Examples 1 to 12 not containing these elements. In the cases other three elements were selected, almost the same results were obtained.

[0099]

It was further confirmed that the thin film piezoelectric devices 10 of Examples 17 to 20 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and containing Mn, Li, Ba, and Ta exhibit lower leakage current densities than those of the thin film piezoelectric devices 10 of Examples 13 to 16 each including the KNN thin film containing only Li, Ba, and Ta but not Mn (comparison between the KNN thin films having substantially the same average crystal grain diameter (± 5%)). In addition, it was confirmed that Examples 17 to 20 have higher piezoelectric constants -d31.

[0100]

It was further confirmed that the thin film piezoelectric devices 10 of Examples 21 to 24 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and containing Mn, Li, Ba, Ta, Sr, and Zr exhibit higher piezoelectric constants -d31 than those of the thin film piezoelectric devices 10 of Examples 17 to 20 each including the KNN thin film having an average crystal grain diameter of 60 nm or more and 90 nm or less and containing Mn, Li, Ba, and Ta.

A piezoelectric actuator according to the present invention includes the thin film piezoelectric device with increased coercive electric field and can improve the deformation characteristics, and a piezoelectric sensor according to the present invention includes the thin film piezoelectric device with increased coercive electric field and can improve the detecting sensitivity. Therefore, a high performance hard disk drive and ink jet printer device can be provided.

[Table 1]

Table 1

| | Additive | Substrate temperature (°C) | KNN film thickness (um) | Average crystal grain diameter (nm) | Area ratio of deposited grains in section (%) | Leakage current density (A/cm$^2$) | -d31 (pm/V) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $V_{pp}3V$ | $V_{pp}20V$ |
| Comparative Example 1 | No | 550 | 2.0 | 320 | 4 | $2.4 \times 10^{-2}$ | 101 | 0 |
| Comparative Example 2 | No | 530 | 2.0 | 95 | 40 | $7.4 \times 10^{-4}$ | 92 | 3 |
| Example 1 | No | 520 | 2.0 | 90 | 42 | $9.9 \times 10^{-7}$ | 89 | 89 |
| Example 2 | No | 510 | 2.0 | 86 | 55 | $6.0 \times 10^{-7}$ | 86 | 86 |
| Example 3 | No | 500 | 2.0 | 83 | 60 | $4.5 \times 10^{-7}$ | 81 | 81 |
| Example 4 | No | 490 | 2.0 | 77 | 66 | $3.8 \times 10^{-7}$ | 79 | 79 |
| Example 5 | No | 480 | 2.0 | 71 | 67 | $3.0 \times 10^{-7}$ | 77 | 77 |
| Example 6 | No | 470 | 2.0 | 65 | 70 | $8.0 \times 10^{-8}$ | 73 | 73 |
| Example 7 | No | 460 | 2.0 | 61 | 81 | $7.2 \times 10^{-8}$ | 70 | 70 |
| Comparative Example 3 | No | 450 | 2.0 | 55 | 87 | $3.2 \times 10^{-8}$ | 26 | 26 |
| | | | | | | | | |
| Comparative Example 4 | Mn | 530 | 2.0 | 92 | 42 | $7.5 \times 10^{-5}$ | 90 | 10 |
| Example 8 | Mn | 520 | 2.0 | 87 | 54 | $7.1 \times 10^{-8}$ | 82 | 82 |
| Example 9 | Mn | 510 | 2.0 | 79 | 56 | $6.9 \times 10^{-8}$ | 77 | 77 |
| Example 10 | Mn | 500 | 2.0 | 75 | 60 | $6.7 \times 10^{-8}$ | 73 | 73 |
| Example 11 | Mn | 490 | 2.0 | 72 | 71 | $2.0 \times 10^{-8}$ | 71 | 71 |
| Example 12 | Mn | 480 | 2.0 | 65 | 74 | $1.1 \times 10^{-8}$ | 70 | 70 |
| Comparative Example 5 | Mn | 470 | 2.0 | 58 | 80 | $5.0 \times 10^{-9}$ | 30 | 30 |
| | | | | | | | | |
| Comparative Example 6 | Li,Ba,Ta | 530 | 2.0 | 93 | 45 | $2.5 \times 10^{-5}$ | 102 | 28 |
| Example 13 | Li,Ba,Ta | 520 | 2.0 | 88 | 58 | $8.0 \times 10^{-7}$ | 96 | 96 |
| Example 14 | Li,Ba,Ta | 490 | 2.0 | 80 | 62 | $5.5 \times 10^{-7}$ | 92 | 92 |
| Example 15 | Li,Ba,Ta | 480 | 2.0 | 72 | 71 | $1.1 \times 10^{-7}$ | 88 | 88 |
| Example 16 | Li,Ba,Ta | 470 | 2.0 | 62 | 84 | $2.5 \times 10^{-8}$ | 80 | 80 |
| Comparative Example 7 | Li,Ba,Ta | 460 | 2.0 | 57 | 90 | $1.0 \times 10^{-8}$ | 38 | 38 |
| | | | | | | | | |
| Comparative Example 8 | Mn,Li,Ba,Ta | 530 | 2.0 | 92 | 48 | $4.5 \times 10^{-6}$ | 110 | 39 |
| Example 17 | Mn,Li,Ba,Ta | 520 | 2.0 | 86 | 59 | $6.2 \times 10^{-8}$ | 100 | 100 |
| Example 18 | Mn,Li,Ba,Ta | 490 | 2.0 | 78 | 63 | $5.2 \times 10^{-8}$ | 98 | 98 |
| Example 19 | Mn,Li,Ba,Ta | 480 | 2.0 | 71 | 74 | $1.0 \times 10^{-8}$ | 95 | 95 |
| Example 20 | Mn,Li,Ba,Ta | 470 | 2.0 | 62 | 88 | $8.0 \times 10^{-9}$ | 89 | 89 |
| Comparative Example 9 | Mn,Li,Ba,Ta | 460 | 2.0 | 55 | 95 | $4.0 \times 10^{-9}$ | 40 | 40 |
| | | | | | | | | |
| Comparative Example 10 | Mn,Li,Sr,Ba,Zr,Ta | 530 | 2.0 | 91 | 49 | $4.0 \times 10^{-6}$ | 121 | 44 |
| Example 21 | Mn,Li,Sr,Ba,Zr,Ta | 520 | 2.0 | 84 | 60 | $6.4 \times 10^{-8}$ | 110 | 110 |
| Example 22 | Mn,Li,Sr,Ba,Zr,Ta | 490 | 2.0 | 76 | 64 | $5.0 \times 10^{-8}$ | 108 | 108 |
| Example 23 | Mn,Li,Sr,Ba,Zr,Ta | 480 | 2.0 | 70 | 75 | $9.0 \times 10^{-9}$ | 102 | 102 |
| Example 24 | Mn,Li,Sr,Ba,Zr,Ta | 470 | 2.0 | 60 | 90 | $7.3 \times 10^{-9}$ | 99 | 99 |
| Comparative Example 11 | Mn,Li,Sr,Ba,Zr,Ta | 460 | 2.0 | 53 | 98 | $3.0 \times 10^{-9}$ | 45 | 45 |

Note) -d31: calculated from a displacement and the values below.
Young's modulus of Si substrate: 168 GPa
Young's modulus of KNN film: 104 GPa
Thickness of Si substrate: 400 μm
Length of drive portion in thin film piezoelectric device: 13.5 mm

## CLAIMS

[Claim 1]

A thin film piezoelectric device comprising a potassium sodium niobate-based piezoelectric thin film which has an average crystal grain diameter of 60 nm or more and 90 nm or less, and a pair of electrode films configured to hold the piezoelectric thin film therebetween.

[Claim 2]

The thin film piezoelectric device according to Claim 1, wherein a sectional structure of the piezoelectric thin film in a direction perpendicular to the electrode films contains a portion where a plurality of grains are present in the thickness direction of the piezoelectric thin film, and a ratio of total sectional area of grains constituting the portion where the plurality of grains are present is 50% or more of a total sectional area of the piezoelectric thin film.

[Claim 3]

The thin film piezoelectric device according to Claim 1, wherein the piezoelectric thin film contains Mn (manganese).

[Claim 4]

The thin film piezoelectric device according to Claim 1, wherein the piezoelectric thin film contains at least three elements selected from Li (lithium), Sr (strontium), Ba (barium), Zr (zirconium), and Ta (tantalum).

[Claim 5]

A piezoelectric actuator comprising the thin film piezoelectric device according to Claim 1.

[Claim 6]

A piezoelectric sensor comprising the thin film piezoelectric device according to Claim 1.

[Claim 7]

A hard disk drive comprising the piezoelectric actuator according to Claim 5.

[Claim 8]

An ink jet printer device comprising the piezoelectric actuator according to Claim 5.

FIG. 1

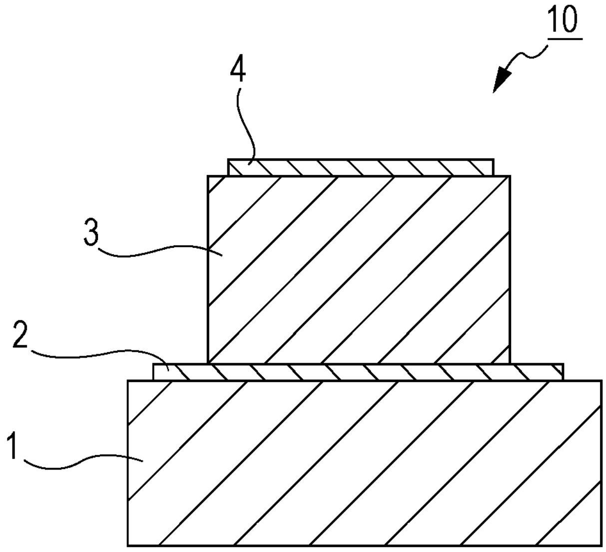


FIG. 2A

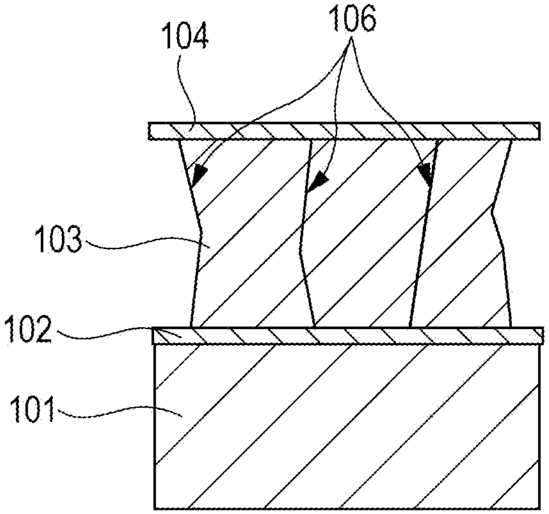
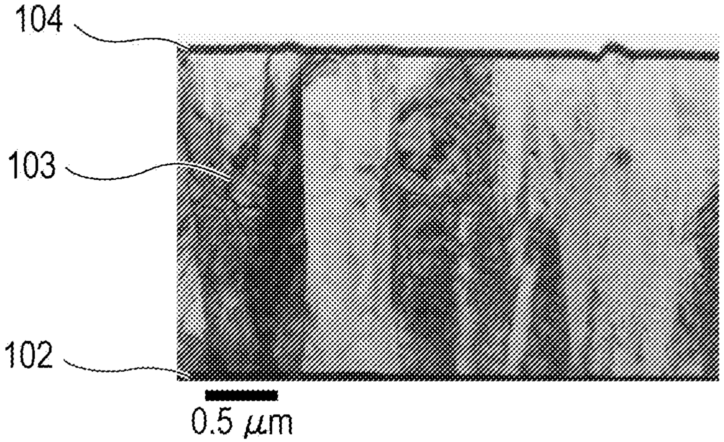


FIG. 2B



(AVERAGE CRYSTAL GRAIN DIAMETER: 350 nm)

FIG. 3A

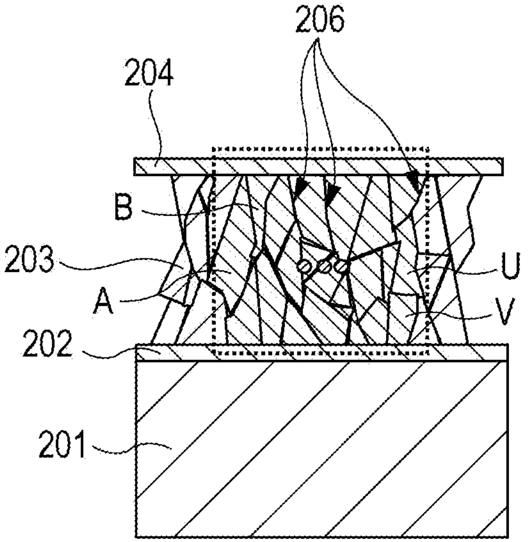


FIG. 3B

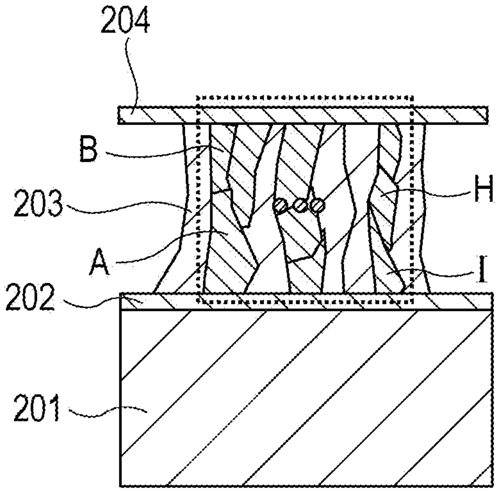
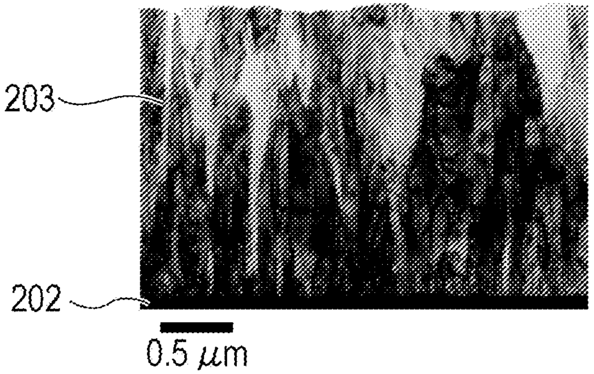


FIG. 3C



(AVERAGE CRYSTAL GRAIN DIAMETER: 80 nm)

FIG. 4

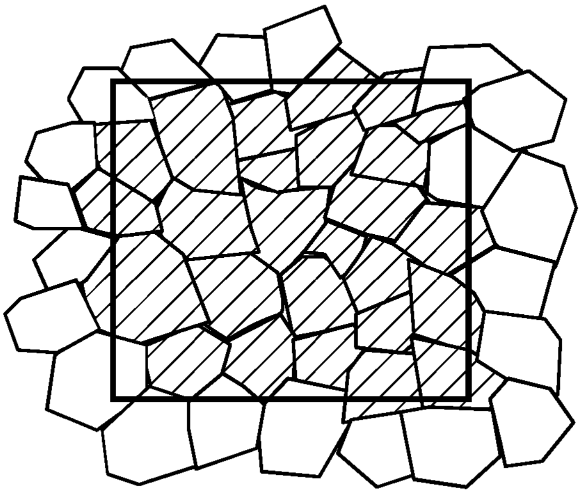
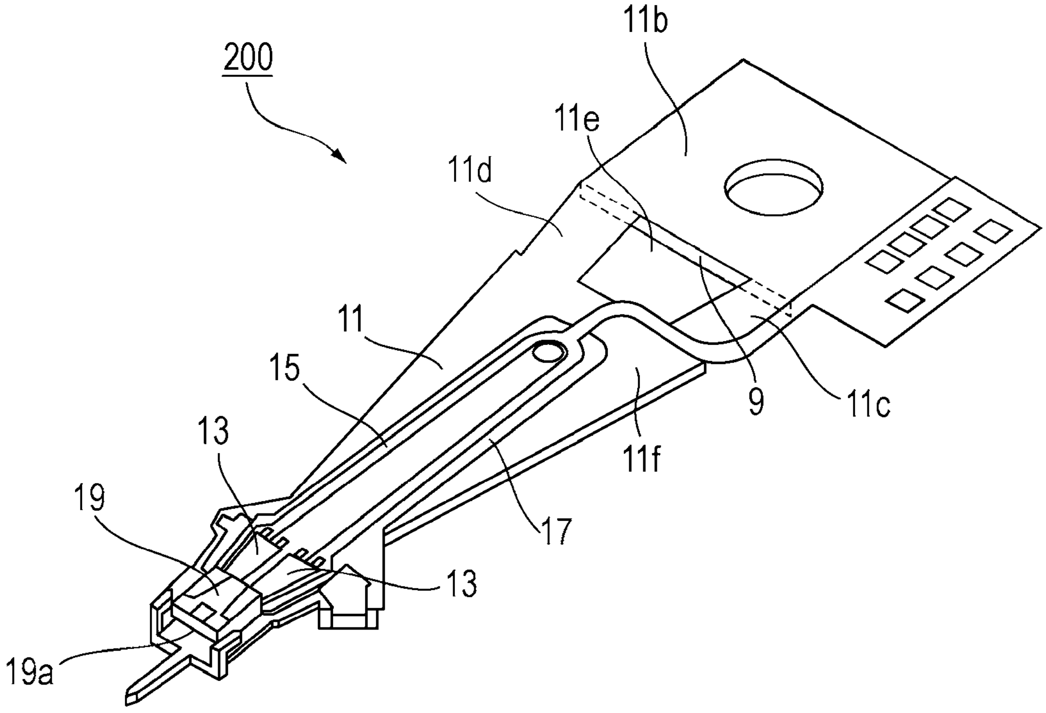


FIG. 5A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11e
11d
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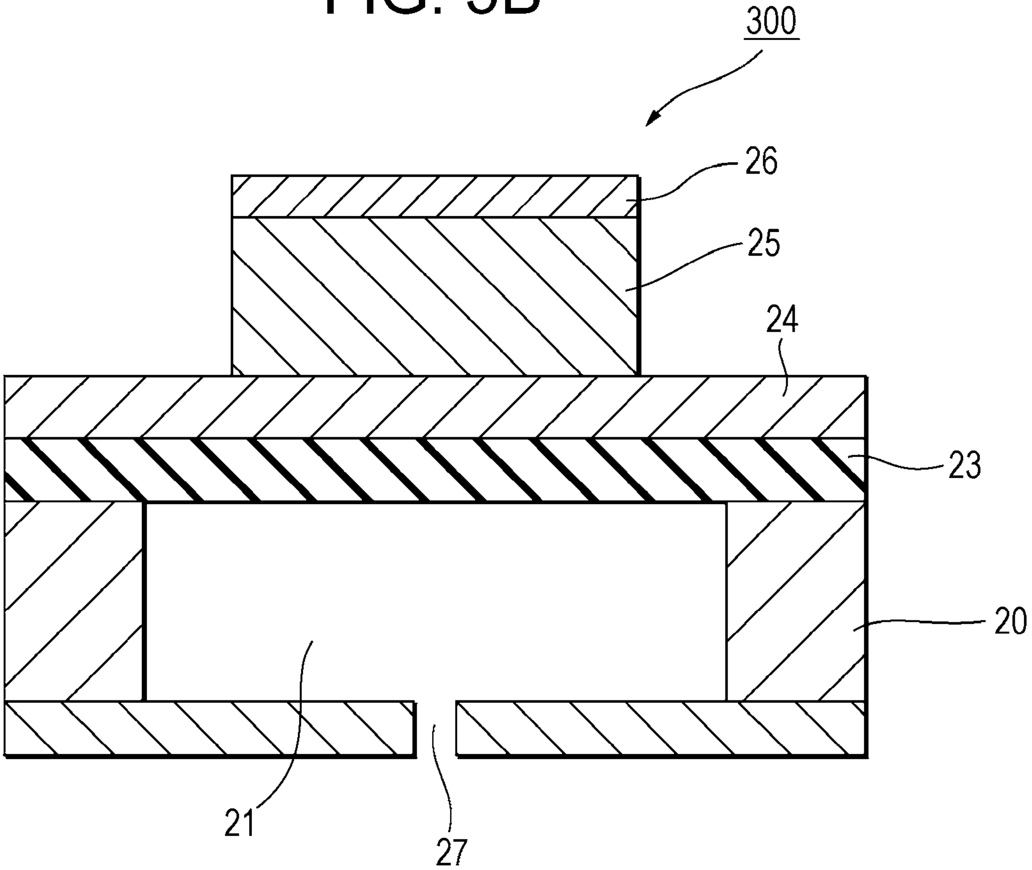
15
13
19
13
19a
9
11c
11f
17

FIG. 5B


300
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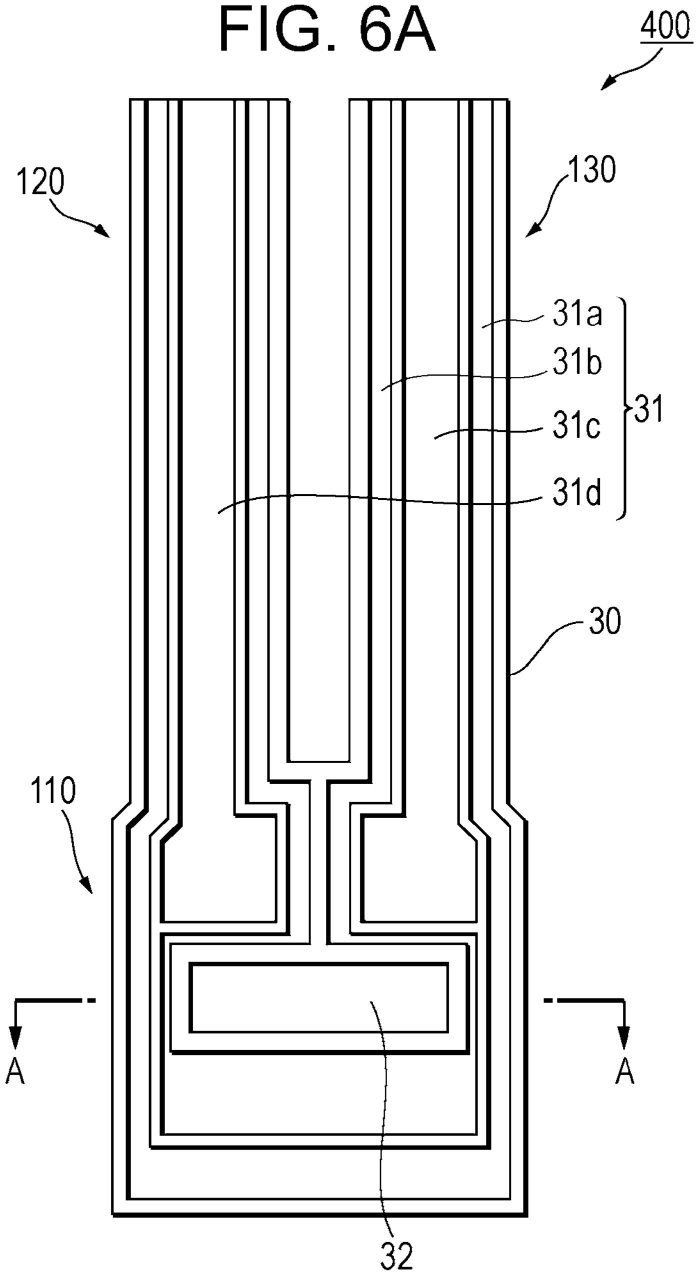
25
24
23
20
21
27

FIG. 6A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31b
31c
31d
31
30
110
A
A
32

FIG. 6B

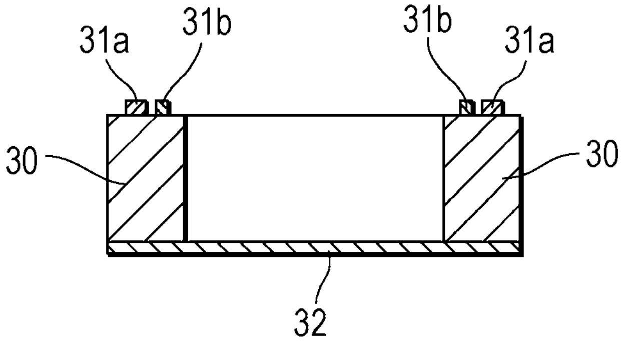
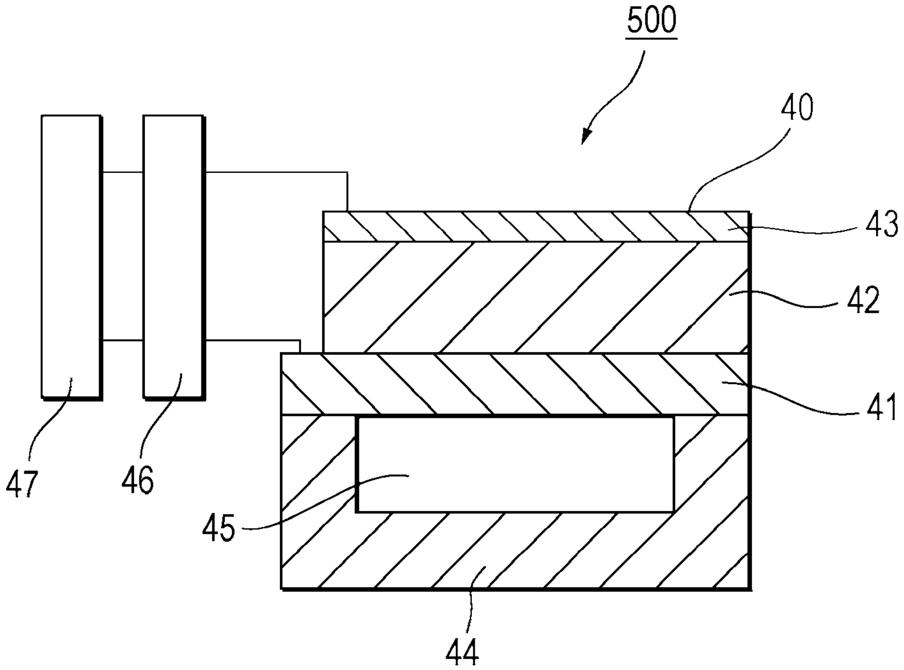

31a
31b
31b
31a
30
30
32

FIG. 6C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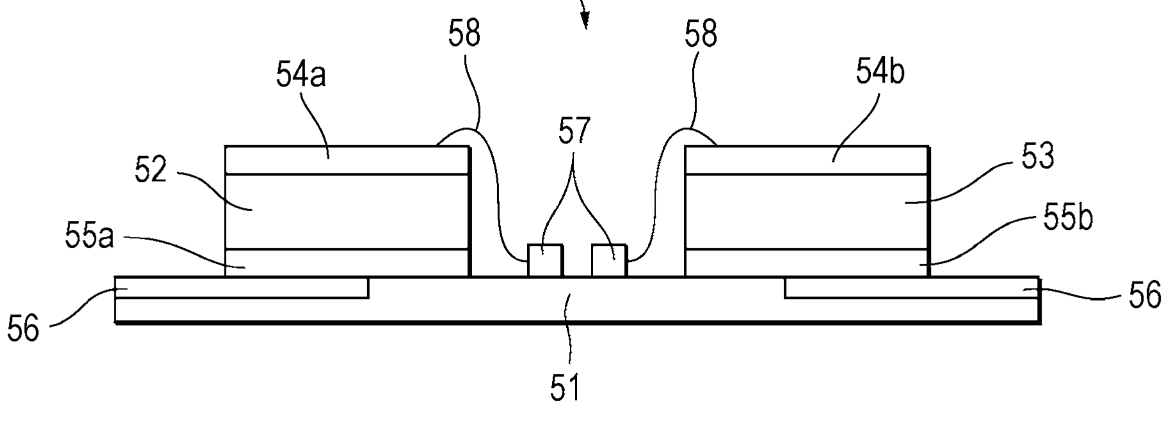
45
44

FIG. 6D


600
58
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54a
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54b
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53
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55b
56
56
51

FIG. 7

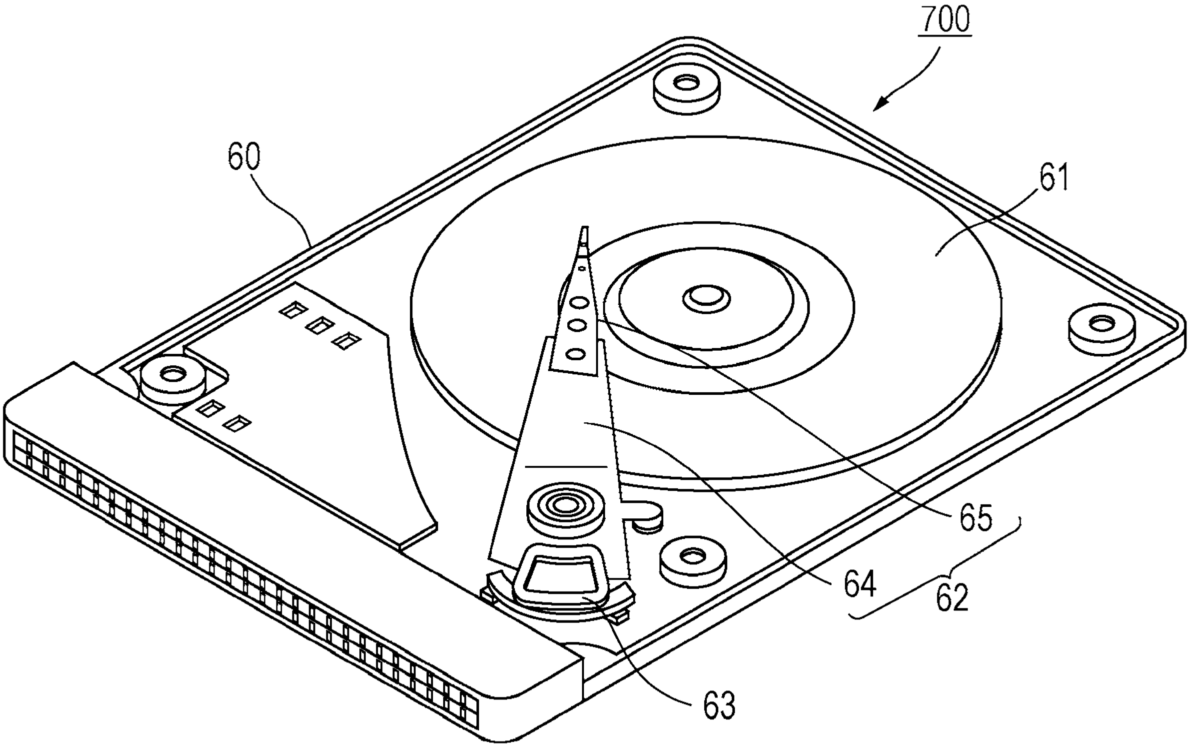
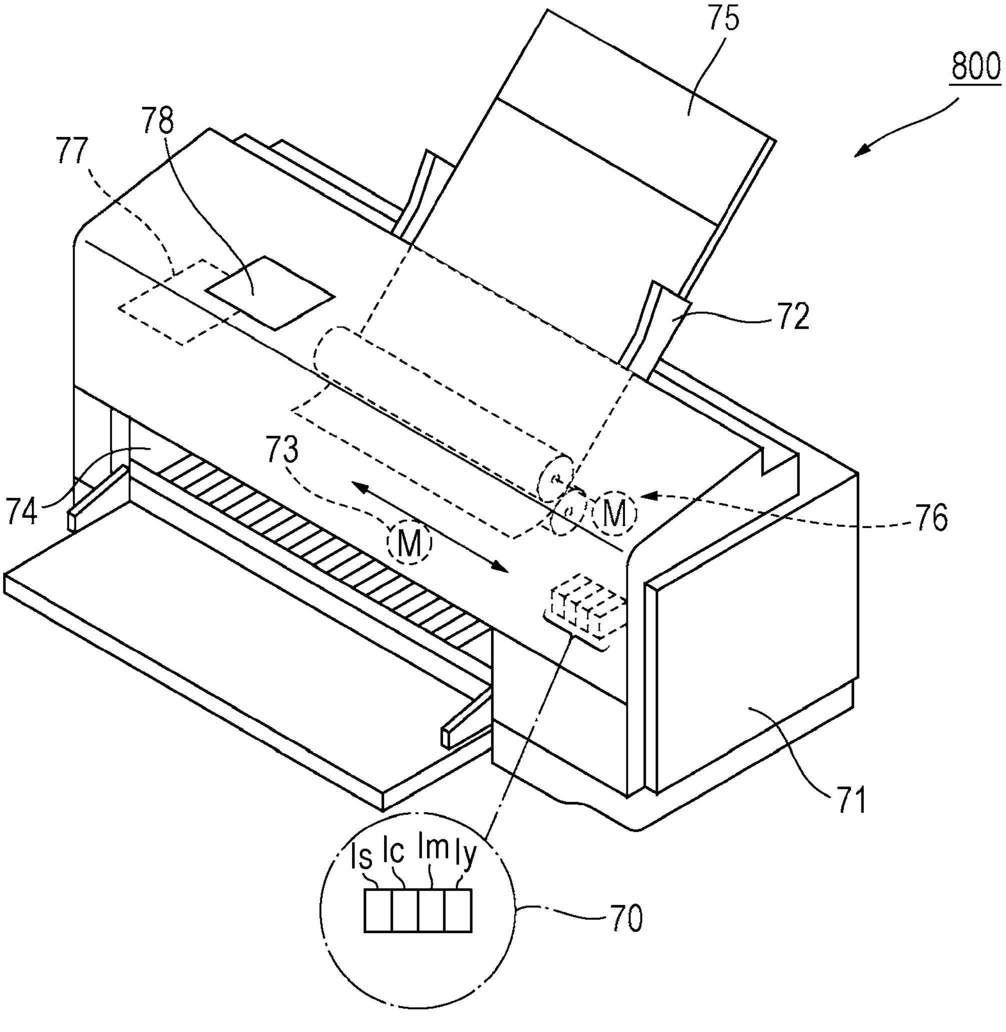


FIG. 8



# INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/002479

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L41/08 H01L41/187 H01L41/316
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L B41J G01C G01L G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | EP 1 965 450 A2 (NGK INSULATORS LTD [JP]) 3 September 2008 (2008-09-03) paragraphs [0002], [0013], [0024] - [0043] | 1-3,5,6, 8<br>7 |
| A | US 2012/025667 A1 (HORIKIRI FUMIMASA [JP] ET AL) 2 February 2012 (2012-02-02) paragraphs [0112] - [0120] | 4 |
| A | EP 1 405 836 A1 (TDK CORP [JP]) 7 April 2004 (2004-04-07) paragraph [0021] - paragraph [0026] | 4 |
| Y | US 2006/066180 A1 (NANATAKI TSUTOMU [JP] ET AL) 30 March 2006 (2006-03-30) paragraph [0075] - paragraph [0078]; figure 13 | 7 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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