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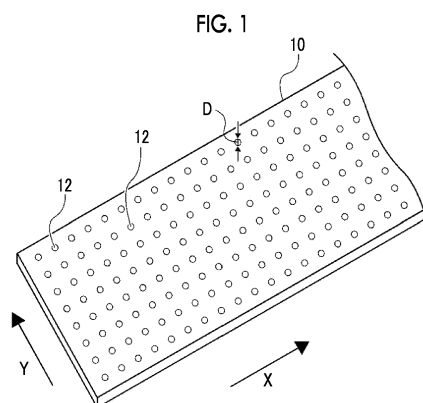
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(54) **METAL FORMED PRODUCT MANUFACTURING METHOD**

(57) Provided is a metal molded product manufacturing method including an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step. In a case where a posture of a surface of the mask which is vertically downward and horizontal is set as a reference posture in a state where the substrate is immersed in water and the surface of the mask is tilted from the reference posture, a movement start angle, which is a tilt angle of the surface of the mask with respect to the reference posture in a case where a bubble of 3 μ L attached to the surface of the mask in the reference posture starts moving along the surface of the mask due to buoyancy, is equal to or less than 20°.



Description**BACKGROUND OF THE INVENTION**

1. Field of the Invention

[0001] The present disclosure relates to a metal molded product manufacturing method.

2. Description of the Related Art

[0002] There is a known metal molded product manufacturing method having a plurality of openings by using an electroforming technique (for example, refer to JP2008-23792A). The metal molded product manufacturing method described in JP2008-23792A is a metal molded product manufacturing method including an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step. The mask is, for example, a photo-sensitive resin.

[0003] JP2008-23792A manufactures a nozzle plate used as a printing head of an inkjet printer as a metal molded product. The nozzle ejects ink to print dots corresponding to pixels that are constituent elements of an image to be printed.

[0004] The nozzle plate is a thin metal plate in which a plurality of openings functioning as nozzles for ejecting ink are one-dimensionally or two-dimensionally arranged. In order to form the plurality of openings arranged in such a manner, JP2008-23792A uses a substrate in which a plurality of masks are one-dimensionally or two-dimensionally arranged on the conductive surface.

[0005] JP2002-80995A describes a method of performing metal wiring in a groove, a through hole, or the like formed in a circuit board by using an electroforming technique. JP2002-80995A describes that a bubble having a diameter of about 100 μm are attached to a surface of a circuit board in an electrolytic solution, and that the attached bubbles cause a lack of a wiring pattern or a decrease in a wire film thickness. As a solution to such a problem, JP2002-80995 describes that bubbles attached to the surface of the circuit board are removed from the surface due to buoyancy by disposing the circuit board in the electrolytic solution in a tilted posture.

SUMMARY OF THE INVENTION

[0006] Each of the plurality of openings of the nozzle plate described in JP2008-23792A functions as a nozzle for ejecting ink. Therefore, it may be necessary for the shapes and sizes of the plurality of openings to have high uniformity. The reason for this is that, in a case where the amount of ink ejected from each nozzle is non-uniform, the sizes of dots corresponding to the pixels of the image to be printed by the printing head are non-uniform, and the image quality is deteriorated. In order to improve the image quality, it is necessary to make the amount of ink, which is ejected from each nozzle, uniform. For that purpose, high dimensional accuracy is necessary for the opening functioning as each nozzle in the nozzle plate.

[0007] In recent years, there is a demand for improvement in image quality, and the resolution of an image tends to be high. In that case, it is necessary to reduce the size of dots. Therefore, it is also necessary to reduce the size of the opening of the nozzle plate to about several tens of μm . In a case where an opening having a diameter of about several tens of μm is formed, in a case where a nozzle plate is manufactured by the method described in JP2008-23792A, for example, a mask having a diameter of about 100 μm is formed on a conductive surface of a substrate. Further, by forming a metal layer growing from the conductive surface so as to cover an edge portion of the peripheral edge of the mask, an opening with a diameter of several tens of μm is formed in the central part of the mask. In a case where a nozzle plate having such a small opening size is manufactured, by simply performing the method described in JP2008-23792A, such molding defects that the sizes and shapes of the plurality of openings are non-uniform may occur.

[0008] As a result of the analysis, the inventor of the present application has determined that attachment of bubbles having a diameter of several tens of μm or less to the non-conductive mask is a major cause of the molding defects of the openings. According to the analysis, the mechanism of the molding defects of the openings caused by the bubbles is presumed as follows. In a case where the bubbles are attached to the mask, the metal layer that grows so as to cover the edge portion of the mask grows while entraining the bubbles. In a case where the metal layer entrains the bubbles, the metal layer containing the bubbles is formed by swelling greater than the other parts. In such a manner, in a case where the metal layer is formed by swelling at the edge portion of the mask, the metal layer swells from the edge portion of the mask toward the central part. As the metal layer bulges toward the center of the mask, the size of the opening decreases in diameter, or the shape of the opening which should be circular is a crescent shape, which causes the

molding defects of the openings.

[0009] As described in JP2002-80995, it is conceivable to tilt the substrate in the electrolytic solution to remove bubbles attached to the surface of the mask from the substrate due to buoyancy. In a case of a relatively large bubble having a diameter of about 100 μm , since the buoyancy is correspondingly large, the bubble can be removed only by tilting the substrate.

[0010] However, in the case of relatively small a bubble having a diameter of several tens of μm or less, since the buoyancy is relatively small, there is a problem that, by simply tilting the substrate, the bubble cannot be sufficiently removed from the surface of the mask and the molding defect of the opening cannot be suppressed.

[0011] The present disclosure is made in view of the above circumstances, and it is an object of the present invention to provide a metal molded product manufacturing method capable of suppressing molding defects of openings caused by bubbles having a diameter of several tens of μm or less in a case where a metal molded product having openings is manufactured by electroforming using a substrate having a mask.

[0012] According to a first aspect of the present disclosure, there is a metal molded product manufacturing method comprising an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step.

[0013] In a case where a posture of a surface of the mask which is vertically downward and horizontal is set as a reference posture in a state where the substrate is immersed in water and the surface of the mask is tilted from the reference posture, a movement start angle, which is a tilt angle of the surface of the mask with respect to the reference posture in a case where a bubble of 3 μL attached to the surface of the mask in the reference posture starts moving along the surface of the mask due to buoyancy, is equal to or less than 20° .

[0014] In the first aspect of the present disclosure, it is preferable that in a case where the respective movement start angles of the surface of the mask and the conductive surface are compared under the same condition, the movement start angle of the surface of the mask is smaller.

[0015] In the first aspect of the present disclosure, it is preferable that regarding a contact angle of the bubble of 3 μL attached to the surface of the mask in the reference posture immediately before the bubble starts moving by tilting the surface of the mask from the reference posture, assuming that the contact angle on a side in a movement direction in which the bubble moves due to buoyancy is a first contact angle and the contact angle on a side opposite to the movement direction is a second contact angle, an angular difference, which is a difference between the first contact angle and the second contact angle, is equal to or less than 30° .

[0016] According to a second aspect of the present disclosure, there is a metal molded product manufacturing method comprising an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step.

[0017] In a case where a posture of a surface of the mask which is vertically downward and horizontal is set as a reference posture in a state where the substrate is immersed in water, regarding a contact angle of the bubble of 3 μL attached to the surface of the mask in the reference posture immediately before the bubble starts moving by tilting the surface of the mask from the reference posture, assuming that the contact angle on a side in a movement direction in which the bubble moves due to buoyancy is a first contact angle and the contact angle on a side opposite to the movement direction is a second contact angle, an angular difference, which is a difference between the first contact angle and the second contact angle, is equal to or less than 30° .

[0018] In the first and second aspects of the present disclosure, it is preferable that in a case where the respective angular differences of the surface of the mask and the conductive surface are compared under the same condition, the angular difference of the surface of the mask is smaller.

[0019] In the first and second aspects of the present disclosure, it is preferable that a contact angle of the bubble attached to the mask in the reference posture is equal to or greater than 130° .

[0020] It is preferable that in a case where the respective contact angles of the surface of the mask and the conductive surface in the reference posture are compared under the same condition, the contact angle of the surface of the mask is greater.

[0021] In the first and second aspects of the present disclosure, it is preferable that a hydrophilic treatment is performed on the mask before the electroforming step.

[0022] It is preferable that the hydrophilic treatment is a plasma treatment or an ultraviolet ozone treatment.

[0023] In the first and second aspects of the present disclosure, a non-conductive material which is a material of the mask may be a metal oxide.

[0024] In the first and second aspects of the present disclosure, a non-conductive material which is a material of the mask may be a photosensitive resin.

[0025] In the first and second aspects of the present disclosure, in a case where the conductive material is a photosensitive resin, it is preferable that the metal molded product manufacturing method further comprises a mask forming step of forming a mask on the conductive surface. It is preferable that the mask forming step includes a coating step of uniformly coating the conductive surface with the photosensitive resin, an exposure step of exposing the photosensitive resin in accordance with a pattern of the mask, and a development step of developing the photosensitive resin which is exposed, and a hydrophilic treatment is performed on the photosensitive resin before the development step.

[0026] The hydrophilic treatment may be performed after the exposure step or before the exposure step.

[0027] In the first and second aspects of the present disclosure, it is preferable that in the electroforming step, the substrate is disposed in the electrolytic solution in a posture in which the conductive surface having the mask is vertically downward.

[0028] It is preferable that in the posture in which the conductive surface is vertically downward, a tilt angle of the conductive surface having the mask with respect to the horizontal direction is equal to or less than 60°.

[0029] In the first and second aspects of the present disclosure, it is preferable that the electroforming step is performed while the substrate is rotated around an axis extending in a normal direction from a center position in a plane of the conductive surface.

[0030] In the first and second aspects of the present disclosure, it is preferable that the electroforming step is performed while the electrolytic solution is flowed in a direction in which a fluid pressure of the electrolytic solution is applied toward the conductive surface having the mask.

[0031] In the first and second aspects of the present disclosure, the metal molded product may be a nozzle plate used for a printing head of an inkjet printer.

[0032] Provided is a method for manufacturing a metal molded product capable of suppressing molding defects of openings due to a bubble having a diameter of 10 μm or less in a case of manufacturing a metal molded product having openings by electroforming using a substrate having a mask.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

Fig. 1 is a perspective view showing an example of a metal molded product.

Fig. 2 is a plan view showing a substrate on which a mask is formed.

Fig. 3 is a plan view showing the entire substrate.

Fig. 4 is a diagram showing a manufacturing step of a nozzle plate.

Fig. 5 is a diagram showing an example of an electroforming apparatus.

Fig. 6 is an explanatory diagram of a movement start angle of a bubble.

Fig. 7 shows an electron microscope image showing a defect of a nozzle part on a surface of a nozzle plate.

Fig. 8 shows an electron microscope image showing the defect of the nozzle part on the surface of the nozzle plate.

Fig. 9 shows an electron microscope image showing a nozzle part on a rear surface of the nozzle plate.

Fig. 10 shows an enlarged electron microscope image of the part of the rear surface of the nozzle plate shown in Fig. 9.

Fig. 11 is an explanatory diagram for measuring a contact angle of a bubble.

Fig. 12 is an explanatory diagram of a first contact angle and a second contact angle of the bubble.

Fig. 13 is a diagram showing an example of a mask forming step.

Fig. 14 is a diagram showing another example of the mask forming step.

Fig. 15 is a graph showing a contact angle of a bubble in each film.

Fig. 16 is a graph showing a movement start angle in each film.

Fig. 17 is a diagram schematically showing a shape of a bubble in each film during measurement of an angular difference. Fig. 17A shows a shape of the bubble in a Ni sputter film. Fig. 17B shows a shape of a bubble on a photosensitive resin film which is not subjected to a hydrophilic treatment. Fig. 17C shows a shape of a bubble on the photosensitive resin film which is subjected to the hydrophilic treatment.

Fig. 18 shows a measurement result of a nozzle opening diameter of a nozzle plate of Example 1.

Fig. 19 shows a measurement result of a nozzle opening diameter of a nozzle plate of a comparative example.

Fig. 20 shows a measurement result of a nozzle opening diameter of a nozzle plate of

Example 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0034] Hereinafter, embodiments of the present disclosure will be described with reference to the drawings.

[0035] Fig. 1 is a diagram showing an example of a metal molded product manufactured by a metal molded product manufacturing method according to an embodiment. In the present example, the metal molded product is a nozzle plate 10 used for a printing head of an inkjet printer.

[0036] The nozzle plate 10 is a plate-like member having a rectangular planar shape which is formed of an electroforming metal such as nickel (Ni). The nozzle plate 10 is formed with a plurality of substantially circular openings 12 (hereinafter, referred to as nozzles 12) that function as nozzles and are two-dimensionally arranged. Each nozzle 12 is formed in a substantially circular shape, and a diameter D thereof is, for example, equal to or less than 100 μm , and preferably in a range of 20 μm to 50 μm . In the printing head, the nozzle plate 10 is disposed in a posture in which the long side direction corresponds to a main scanning direction X of the inkjet printer and the short side direction corresponds to a sub-scanning direction Y. A length of the nozzle plate 10 in the main scanning direction is 100 mm as an example, and a length of the nozzle plate 10 in the sub-scanning direction is 40 mm as an example. Further, in the present example, eight nozzle rows including 130 nozzles 12 arranged at regular intervals in the main scanning direction X of the nozzle plate 10 are provided in the sub-scanning direction Y.

[0037] A metal molded product manufacturing method according to a first embodiment will be described. The metal molded product manufacturing method according to the first embodiment includes an electroforming step that uses a substrate in which a non-conductive mask is formed on a part of a conductive surface. In the electroforming step, in a state where the substrate is immersed in the electrolytic solution, a metal layer is grown on the conductive surface by a metal precipitated from the electrolytic solution, and an opening is formed at a position corresponding to the mask. By performing the electroforming step, a metal molded product having the opening is manufactured. In the present example, the manufacturing method of manufacturing the nozzle plate 10 as the metal molded product will be described.

[0038] Fig. 2 is a plan view showing a part of a substrate 20 used as a master in a case where the nozzle plate 10 is formed by electroforming. The substrate 20 has a conductive surface 20a. A metal layer to be the nozzle plate 10 grows on the conductive surface 20a of the substrate 20. Since the nozzle plate 10 is provided with the nozzle 12, a circular mask 25 is formed on the substrate 20 at a position corresponding to a nozzle forming position where the nozzles 12 are formed on the conductive surface 20a. The mask 25 is formed of a non-conductive material. Therefore, the metal does not grow in the part of the mask 25 and an opening is formed, and the nozzles 12 are formed. In the present example, 130 masks 25 in eight rows are formed in a region of 100 mm $\times$ 40 mm of the substrate 20 corresponding to an arrangement pitch and the number of the nozzles 12 of the nozzle plate 10 described above. A diameter D_M of the mask 25 is greater than the diameter D of the nozzle 12, and is, for example, in a range of 150 μm to 200 μm . A thickness of the mask 25 is, for example, 2 μm . In the present example, the masks 25 are formed on the flat substrate 20, the masks 25 are projected with respect to the conductive surface 20a of the substrate 20. Fig. 3 is a plan view showing the entire substrate 20. As shown in Fig. 3, the substrate 20 is, for example, a disk-shaped substrate which has a diameter of 200 mm. The substrate 20 includes the masks 25 of 130 pieces $\times$ 8 rows shown in Fig. 2 in the nozzle plate formation regions A, B, and C which has a size of 100 mm $\times$ 40 mm. The nozzle plate formation regions A, B, and C are disposed in a three-fold rotational symmetry with a normal line that passes through a center 20c of the substrate 20 as a rotational axis. That is, in the substrate 20, the three nozzle plate formation regions A, B, and C are disposed at intervals of 120° with the normal line as the rotational shaft.

[0039] For example, the substrate 20 is provided with a metal film 22 on a glass wafer 21. The surface of the metal film 22 is the conductive surface 20a of the substrate 20. The non-conductive mask 25 is formed on a part of the conductive surface 20a (refer to Fig. 4).

[0040] Fig. 4 is a diagram showing a manufacturing step of the nozzle plate 10. Fig. 4 shows a cross unit of a part of the substrate 20 shown in Fig. 2 including only one mask 25. First, in the provision step S0, the substrate 20 in which the non-conductive mask 25 is formed on a part of the conductive surface 20a is provided. Then, in the electroforming step S1, in a state where the substrate 20 is immersed in the electrolytic solution, the metal layer 11 is grown on the conductive surface 20a by the metal precipitated from the electrolytic solution.

[0041] During electroforming, the metal layer 11 grows on the conductive surface 20a, whereas no metal is precipitated on the surface of the non-conductive mask 25, and the metal layer 11 does not grow. The metal layer 11 gradually grows on the conductive surface 20a. Thereafter, in a case where a thickness of the grown metal layer 11 is greater than a thickness of the mask 25, the metal layer 11 grows on the non-conductive mask 25 side from the surface of the previously grown metal layer 11 so as to cover the edge portion of the mask 25. As the metal layer 11 grows from the edge portion of the mask 25 toward the center, an opening is formed in the metal layer 11 with the opening center at a substantially center position of the mask 25. The opening is the nozzle 12. As the thickness of the metal layer 11 increases, the metal layer 11 grows toward the center of the mask 25. Therefore, the opening diameter of the nozzle 12 also gradually

decreases. The diameter of the mask 25 is determined such that the nozzle 12 has a desired opening diameter in a case where the metal layer 11 is grown to have a desired thickness. The growth of the metal layer 11 on the mask 25 is larger at a position closer to the conductive surface 20a. Therefore, as shown in Fig. 4, the opening diameter of the nozzle 12 is smaller at a position closer to the conductive surface 20a and is larger at a position away from the conductive surface 20a. The cross unit of the metal layer 11 forming an inner wall surface of the nozzle 12 is arc-shaped. For example, as a reference of a target opening diameter of the nozzle 12, the opening diameter of the nozzle 12 close to the conductive surface 20a is set. Then, the diameter of the mask 25 is determined such that the opening diameter of the reference nozzle 12 is the target opening diameter. The thickness t of the metal layer 11 is, for example, about 50 μm .

[0042] After the electroforming step, the metal layer 11 is peeled off from the substrate 20 (peeling step S2). In such a case, the mask 25 is peeled off from the substrate 20 together with the metal layer 11.

[0043] Thereafter, the mask 25 is removed (mask removal step S3). Thereby, it is possible to obtain the nozzle plate 10.

[0044] The electroforming step S1 will be described in detail. Fig. 5 shows an example of the electroforming apparatus 30 used in the electroforming step S1. The electroforming apparatus 30 comprises an electroforming tank 32, a substrate holding mechanism 35, an anode 39, and a circulation mechanism 40 of an electrolytic solution 34.

[0045] The electroforming tank 32 stores the electrolytic solution 34. The anode 39 is disposed on a part of the inner wall surface of the electroforming tank 32. During electroforming, the substrate 20 is immersed in the electrolytic solution 34 of the electroforming tank 32. The substrate 20 is disposed in the electrolytic solution 34, in a posture in which the conductive surface 20a faces the anode 39. The anode 39 is configured to include an electroforming metal such as nickel pellets and has a size by which the anode 39 is capable of facing the entire region of the conductive surface 20a on the substrate 20. Electroforming is performed on the substrate 20 in a state where the conductive surface 20a of the substrate 20 faces the anode 39.

[0046] In the present example, a part of the side wall of the electroforming tank 32 is tilted. The tilt direction of the side wall is a direction in which the upper opening becomes wider than the opening on the bottom surface of the electroforming tank 32 due to the tilt of the side wall. The tilt angle of the side wall is, for example, in a range of about 40° to about 50° with respect to the horizontal direction. The anode 39 is disposed along the inner wall surface of the tilted side wall in a tilted posture with respect to the horizontal direction.

[0047] The substrate holding mechanism 35 includes a holding part 36, a rotational shaft 37, and a rotation device 38. The holding part 36 holds the substrate 20 from the opposite surface side of the conductive surface 20a of the substrate 20. The rotational shaft 37 is attached to the rear surface of the holding part 36 and extends in the normal direction of the rear surface of the holding part 36. The rotation device 38 rotates the holding part 36 through the rotational shaft 37. The holding part 36 holds the substrate 20 in the electroforming tank 32 such that the conductive surface 20a of the substrate 20 faces the anode 39. That is, in the substrate 20, the conductive surface 20a is disposed in a vertically downward posture. Here, the vertically downward posture means a posture in which the tilt angle of the conductive surface 20a with respect to the horizontal direction is equal to or greater than 0° and less than 90°. In the present example, the tilt angle is greater than 0°, and the conductive surface 20a is disposed in a posture in which the conductive surface 20a is horizontally tilted.

[0048] The holding part 36 holds the substrate 20 by such that the center coincides with the rotational shaft 37. In a case where the rotation device 38 is driven, the substrate 20 rotates integrally with the holding part 36 through the rotational shaft 37, with the center coinciding with the rotational shaft 37 as the center of rotation. The substrate 20 is set in the holding part 36 outside the electroforming tank 32, and is immersed in the electroforming tank 32 in a state of being held by the holding part 36. Then, electroforming is performed while the substrate 20 is rotated about an axis extending in the normal direction from a center position in the plane of the conductive surface 20a.

[0049] During electroforming, the conductive surface 20a of the substrate 20 is used as a cathode, and the conductive surface 20a serving as a cathode and the anode 39 including the electroforming metal are energized. Thereby, the electroforming metal of the anode 39 is electrolyzed and is dissolved in the electrolytic solution 34 as electric ions. Then, the metal layer 11 is formed by electrodepositing the metal precipitated from the electrolytic solution 34 on the conductive surface 20a serving as a cathode.

[0050] The circulation mechanism 40 includes a reservoir 41, a discharge pipe 42, a valve 43, a pump 44, a filter 46, a supply pipe 47, and a nozzle 48. The circulation mechanism 40 circulates the electrolytic solution 34 stored in the electroforming tank 32 between the electroforming tank 32 and the reservoir 41 disposed outside the electroforming tank 32. Through the circulation, the electrolytic solution 34 is made to flow between the conductive surface 20a and the anode 39.

[0051] The discharge pipe 42 and the supply pipe 47 form a circulation passage for the electrolytic solution 34 between the electroforming tank 32 and the reservoir 41. The discharge pipe 42 constitutes a returning pipe line in which the electrolytic solution 34 in the electroforming tank 32 is discharged and the discharged electrolytic solution 34 is returned to the reservoir 41 through the circulation passage. The supply pipe 47 constitutes a supply pipe line for supplying the electrolytic solution 34 from the reservoir 41 to the electroforming tank 32 in the circulation passage.

[0052] One end of the discharge pipe 42 is disposed in the electroforming tank 32, and the other end thereof is

connected to the reservoir 41. Through the discharge pipe 42, the electrolytic solution 34, which has an amount greater than a preset specified amount in the electroforming tank 32, is returned to the reservoir 41. Therefore, one end of the discharge pipe 42 is disposed at substantially the same height as the liquid surface of the specified amount of the electrolytic solution 34 with the opening facing upward. Thereby, the electrolytic solution 34 in excess of the specified amount in the electroforming tank 32 flows into the discharge pipe 42 and is returned to the reservoir 41 through the discharge pipe 42.

[0053] One end of the supply pipe 47 is also disposed in the electroforming tank 32, and the other end thereof is connected to the reservoir 41. The nozzle 48, through which the electrolytic solution 34 is injected into the electroforming tank 32, is connected to one end of the supply pipe 47. The other end of the supply pipe 47 is connected to the lower part of the reservoir 41. The valve 43, the pump 44, and the filter 46 are disposed on the supply pipe line constituted of the supply pipe 47 in order from the reservoir 41 side which is the upstream side of the electrolytic solution 34 in the supply direction. The valve 43 opens and closes a supply passage. In a case where the supply passage is opened through the valve 43 in a state where the pump 44 is driven, the supply of the electrolytic solution 34 from the reservoir 41 to the electroforming tank 32 is started. The filter 46 filters the electrolytic solution 34. The electrolytic solution 34 that passes through the filter 46 is supplied into the electroforming tank 32 through the supply pipe 47. Through the nozzle 48, the electrolytic solution 34 is injected toward between the conductive surface 20a of the substrate 20 and the anode 39.

[0054] As described above, in the electroforming step S 1, the electrolytic solution 34 is circulated between the electroforming tank 32 and the reservoir 41 by using the circulation mechanism 40. Then, in the electroforming tank 32, the electrolytic solution 34 is injected from the nozzle 48 toward between the conductive surface 20a and the anode 39. Thereby, the electrolytic solution 34 is flowed in a direction in which the fluid pressure of the electrolytic solution 34 is applied toward the conductive surface 20a having the mask 25. The electroforming step S 1 is performed while the electrolytic solution 34 is flowed in such a manner.

[0055] As described above, the electroforming is performed on the conductive surface 20a of the substrate.

[0056] In the present embodiment, as the substrate 20 on which the non-conductive mask 25 is formed, a substrate in which a movement start angle of a bubble attached to the surface of the mask 25 is equal to or less than 20° is used. The movement start angle is one of indicators indicating the surface characteristics of the mask 25, and is defined herein as follows. The movement start angle is a tilt angle of the surface of the mask 25 with respect to the reference posture in a case where a bubble of 3 microliters (μL) attached to the mask 25 starts moving along the surface of the mask 25 due to buoyancy, in a case where a surface of the mask 25 is vertically downward and a horizontal posture is set as a reference posture in a state where the substrate 20 is immersed in water and the surface of the mask 25 is tilted from the reference posture. The surface of the mask 25 is parallel with the conductive surface 20a of the substrate 20 on which the mask 25 is formed. Therefore, the above-mentioned reference posture is obtained in a case where the substrate 20 is disposed such that the conductive surface 20a is vertically downward and is in a horizontal posture.

[0057] Here, the movement start angle will be specifically described with reference to Fig. 6.

[0058] As shown in the upper part of Fig. 6, a base material S, which is a parallel plate having two main surfaces s1 and s2 parallel to each other, is disposed in water such that one main surface s1 is vertically downward and is horizontal. Specifically, first, a fixing base 54 for fixing the base material S is immersed in water, and the fixing base 54 is provided such that a fixing surface 54a of the fixing base 54 is horizontal in water. The fixing base 54 is disposed such that the other main surface s2 of the base material S comes into contact with the fixing surface 54a. Thereby, the base material S is disposed in the reference posture. Next, in the reference posture, the main surfaces s1 and s2 of the base material S are horizontal planes. The bubble 50 of 3 μL is brought into contact with the main surface s1 of the base material S. A dispensing nozzle (not shown in the drawing) is disposed below the main surface s1 of the base material S, and air of 3 μL is discharged toward the base material S. Thereby, the bubble 50 of 3 μL is generated, and the generated bubble 50 is brought into contact with the main surface s1 of the base material S.

[0059] After the bubble 50 is attached to the main surface s1, the base material S is gradually tilted together with the fixing base 54 and the fixing surface 54a from the reference posture shown in the upper part of Fig. 6. In such a case, the angle formed by the fixing surface 54a in a case where the bubble 50 starts moving along the main surface s1 of the base material S in the horizontal direction is measured. The main surface s1 of the base material S is parallel with the fixing surface 54a. Therefore, the measured angle of the fixing surface 54a is an angle of the main surface s1 of the base material S, and corresponds to the movement start angle in a case where the bubble 50 starts moving along the main surface s1. Specifically, using a camera of a contact angle measurement device, a state in which the base material S is gradually tilted together with the fixing base 54 is captured from the horizontal direction. Then, an angle formed between the fixing surface 54a and the horizontal direction is obtained through image analysis from an image in a case where the bubble 50 starts moving along the main surface s1 of the base material S.

[0060] The measurement of the angle formed between the fixing surface 54a and the horizontal direction in a case where the bubble 50 starts moving along the main surface s1 is performed, for example, at least three times, and an average value thereof is set as the movement start angle θ of the bubble with respect to the base material. The water

used for the measurement is distilled water, and the bubble is an air bubble. By replacing the surface of the base material S with the mask 25, the movement start angle θ of the bubble with respect to the surface of the mask 25 can be obtained in a similar manner.

[0061] As described above, the movement start angle θ at which the bubble moves from the surface of the mask 25 is one of the indicators indicating the surface characteristics of the mask 25, and is used as an indication that the bubble 50 is likely to remain on the surface of the mask 25. A larger movement start angle θ means that the bubble 50 is more likely to remain on the surface of the mask 25, and a smaller movement start angle θ means that the bubble 50 is less likely to remain on the surface of the mask 25. In a case where the movement start angle θ of the bubble of 3 μL is equal to or less than 20° , attachability of the bubble 50 to the surface of the mask 25 is low. Therefore, the bubble 50 is likely to move. The bubble 50 of 3 μL corresponds to a spherical bubble 50 having a diameter of 4.6 mm. As the size of the bubble 50 is smaller, the buoyancy is smaller. Therefore, the bubble 50 tends to be less likely to move. According to the study by the inventors of the present disclosure, regarding the surface of the mask 25 in which the movement start angle θ of the bubble 50 of 3 μL is equal to or less than 20° , it is presumed that there is the following effect. Even a minute bubble 50 having a diameter of several tens of μm or less is likely to move, and attachment of the minute bubble 50 to the surface of the mask 25 is suppressed. Further, although the movement start angle θ in water is specified herein, there is a correlation between the movement start angle θ of the bubble 50 in water and the movement start angle θ of the bubble 50 in the electrolytic solution during electroforming. That is, the movement start angle θ in the electrolytic solution is also large in a case where the movement start angle θ in water is large, and the movement start angle θ in the electrolytic solution is also large in a case where the movement start angle θ in water is large. According to the study by the inventors of the present disclosure, it is presumed that there is the following effect. In a case where the movement start angle θ of the bubble 50 of 3 μL on the surface of the mask 25 in water is equal to or less than 20° , it is possible to suppress remaining of the bubble 50 and attachment of the minute bubble 50 having a diameter of several tens of μm or less on the surface of the same mask 25 in the electrolytic solution during electroforming.

[0062] Here, Figs. 7 to 10 show electron beam microscope images showing states of the molding defects of the nozzle 120 in a case where a nozzle plate having the nozzle 120 for an inkjet printer is manufactured by electroforming by a conventional method. Fig. 7 shows an image obtained by observing the nozzle 120 from the front on the growth surface side, and Fig. 8 shows an image obtained by observing the nozzle 120 shown in Fig. 7 from an oblique direction. Originally, the nozzle 120 should have a circular opening shape, but the nozzle 120 in which the molding defect has occurred has a crescentic opening shape as shown in Figs. 7 and 8. In Figs. 7 and 8, a part that appears black is the nozzle 120. The reason why the nozzle 120 has a crescent shape is that a part of the metal layer 11 that grows so as to cover the edge portion of the mask 25 is abnormally swelled as compared with the other part thereof. Fig. 9 shows an image obtained by observing the nozzle 120 shown in Fig. 7 and Fig. 8 from the opposite surface side. In Fig. 9, it is more clearly shown that the opening shape of the nozzle 120 is the crescent shape. Further, in Fig. 9, a region in the white frame defined by the circular white frame surrounding the nozzle 120 having a crescent shape is a region corresponding to the shape of the circular mask 25. In the region, the surface is recessed by a thickness of the mask 25 from the surface around the region.

[0063] Further, in Fig. 9, in the circular region within the white frame, the hole 121 is formed in the vicinity of the nozzle 120 having a crescent shape. A hole 121 is located at a position corresponding to a part where the metal layer is raised on the growth surface side of the metal layer 11. Fig. 10 shows an enlarged image of the hole 121. As shown in Fig. 10, the hole 121 is formed by a cavity formed inside the metal layer 11. That is, as shown in Figs. 7 and 8, it is considered that the abnormally bulging part observed on the growth surface side of the metal layer 11 is caused by formation of a cavity inside. Then, it is presumed that the opening part of the cavity is the hole 121 shown in Figs. 9 and 10. Further, it is considered that the cause of the cavity in the metal layer 11 is the bubble 50 attached to the edge portion of the mask 25. That is, since electroforming is performed in a state where the bubble 50 is attached, the bubble 50 is entrained and the metal layer 11 grows. As a result, a cavity is formed in the metal layer 11, and it is considered that the cavity causes an abnormal swelling of the metal layer 11.

[0064] That is, in a case in which the bubble 50 is not attached to the mask 25, the molding defect of the nozzle 12 can be suppressed. As described above, as the substrate 20 on which the non-conductive mask 25 is formed, the substrate 20 having the following configuration is used. In a case where a posture of a surface of the mask 25 which is vertically downward and horizontal is set as a reference posture in a state where the substrate 20 is immersed in water and the surface of the mask 25 is tilted from the reference posture, a movement start angle, which is a tilt angle of the surface of the mask 25 with respect to the reference posture in a case where the bubble of 3 μL attached to the mask 25 starts moving along the surface of the mask 25 due to buoyancy, is equal to or less than 20° . Since such a substrate 20 is used, the bubble can be easily removed from the surface of the mask 25 as compared with the conventional case. Therefore, the molding defect of the nozzle 12 (an example of the opening of metal molded product) of the nozzle plate 10, which is an example of a metal molded product, can be reduced. In particular, even a minute bubble having a diameter of several tens of μm or less can be easily removed. Therefore, in a case of manufacturing the metal molded product having the nozzles 12 (an example of openings of the metal molded product) of 100 μm or less, such as the nozzle plate

10, there is a high effect of suppressing molding defects of the openings.

[0065] In a case where the movement start angles θ of the surface of the mask 25 and the conductive surface 20a are compared under the same condition, it is preferable to use the substrate 20 in which the movement start angle θ of the surface of the mask 25 is smaller.

[0066] By making the movement start angle of the surface of the mask 25 smaller than that of the conductive surface 20a, as compared with a case where the movement start angles of the surface of the mask 25 and the conductive surface 20a are the same, the bubble 50 is likely to move from the surface of the mask 25 toward the conductive surface 20a. Therefore, it is possible to more reliably reduce molding defects of openings.

[0067] The substrate 20 of the present example has the following configuration. The conductive surface 20a is a flat surface, and the mask 25 is formed on the flat conductive surface 20a. As a result, the mask 25 is disposed to be projected with respect to the conductive surface 20a. However, the mask 25 may be formed at a position lower by one stage than the conductive surface 20a of the substrate 20, and a portion where the mask 25 is formed may be recessed. Further, the heights of the conductive surface 20a and the surface of the mask 25 may be the same, and both surfaces may be coplanar.

[0068] Next, a metal molded product manufacturing method according to a second embodiment will be described. In a similar manner to the first embodiment, the metal molded product manufacturing method according to the second embodiment also includes an electroforming step of using the substrate 20 in which the non-conductive mask 25 is formed on a part of the conductive surface 20a. In the electroforming step, in a state where the substrate 20 is immersed in the electrolytic solution 34, the metal layer 11 is grown on the conductive surface 20a by the metal precipitated from the electrolytic solution 34, and the opening is manufactured at a position corresponding to the mask 25. In the present example as well, a manufacturing method of manufacturing the nozzle plate 10 as the metal molded product will be described. The entire flow of the manufacturing step shown in Fig. 4 is basically the same as that of the first embodiment described above. In the following description, only the differences will be described, and detailed description of the same parts will be omitted.

[0069] In the present embodiment, as the substrate 20 on which the non-conductive mask 25 is formed, the substrate 20 that satisfies the following conditions as the condition about the contact angle of the bubble 50 with respect to the mask 25 is used. First, the contact angle of the bubble 50 is defined as follows. That is, in a case where a posture of a surface of the mask 25 which is vertically downward and horizontal is set as a reference posture in a state where the substrate 20 is immersed in water, regarding a contact angle of the bubble 50 immediately before the bubble 50 of 3 μ L attached to the surface of the mask 25 in the reference posture starts moving by tilting the surface of the mask 25 from the reference posture, it is assumed that the contact angle on a side in a movement direction in which the bubble 50 moves due to buoyancy is a first contact angle ϕ_1 and the contact angle on a side opposite to the movement direction is a second contact angle ϕ_2 . In such a case, as the substrate 20, the substrate 20 in which an angular difference $\Delta\phi = \phi_2 - \phi_1$ which is the difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 is equal to or less than 30° is used.

[0070] Here, the contact angle ϕ , the first contact angle ϕ_1 , and the second contact angle ϕ_2 of the bubble 50 will be described with reference to Figs. 11 and 12.

[0071] First, a measuring method of the contact angle ϕ of the bubble 50 will be described. As shown in Fig. 11, first, the base material S, which is a parallel plate having two main surfaces s1 and s2 parallel to each other, is disposed in water in a water tank, in which water 52 is stored, such that one main surface s1 is vertically downward and horizontal. Specifically, the fixing base 54 (not shown in Fig. 11) shown in Fig. 6 is used and is disposed such that the other main surface s2 of the base material S comes into contact with the fixing surface 54a. Thereby, the base material S is disposed in the reference posture. Next, in the reference posture, the main surfaces s1 and s2 of the base material S are horizontal planes. The bubble 50 of 3 μ L is brought into contact with the main surface s1 of the base material S.

[0072] The contact angle ϕ of the bubble 50 means an angle between the base material S and the tangent line of the bubble 50 at the end part where the bubble 50 is in contact with the base material S in a case where the bubble 50 being in contact with the base material S is observed from the horizontal direction. Specifically, a camera of a contact angle measurement device is used to image the horizontally disposed base material S and the bubble 50 being in contact with the surface of the base material S from the horizontal direction. Thereby, the angle formed between the tangent line of the bubble 50 and the base material S is obtained through the image analysis. The measurement is performed, for example, at least three times, and an average value thereof is set as the contact angle ϕ . By replacing the surface of the base material S with the mask 25, the contact angle ϕ of the bubble with respect to the surface of the mask 25 can be obtained in a similar manner.

[0073] Next, the first contact angle ϕ_1 and the second contact angle ϕ_2 will be described. As shown in Fig. 12, the first contact angle ϕ_1 is a contact angle on a side of the movement direction in which the bubble 50 moves at the above-mentioned movement start angle θ (refer to Fig. 6), and the contact angle is also referred to as a forward contact angle. Further, the second contact angle ϕ_2 is a contact angle on a side opposite to the movement direction in which the bubble moves immediately before the movement start angle, and the contact angle is also referred to as a backward contact

angle. In a similar manner to the case of the movement start angle θ shown in Fig. 6, the bubble 50 of 3 μL is attached to the surface of the base material S, and together with the fixing base 54, the base material S is tilted from the reference posture (not shown in Fig. 12, refer to Fig. 6), in a direction in which an angle formed between the fixing surface 54a and the horizontal plane increases. In such a case, the contact angle of the bubble 50 is measured in a case where the tilt angle of the main surface s1 of the base material S with respect to the horizontal direction is the movement start angle θ , that is, immediately before the bubble 50 starts moving. Specifically, using a camera of a contact angle measurement device, a state in which the base material S is gradually tilted together with the fixing base 54 is imaged from a horizontal direction, and an angle, which is formed between the base material S and the tangent line at the end part on the side of the movement direction of the bubble in an image immediately before the bubble 50 leave the base material S, and an angle, which is formed between the base material S and the tangent line at the end part on the side opposite to the movement direction of the bubble 50 are obtained through the image analysis.

[0074] The measurement is performed at least three times for each angle, and the average values thereof are set as the first contact angle φ_1 and the second contact angle φ_2 , respectively. The angular difference $\Delta\varphi$ between the first contact angle φ_1 and the second contact angle φ_2 obtained in such a manner is obtained.

[0075] The angular difference $\Delta\varphi$ between the first contact angle φ_1 and the second contact angle φ_2 at the movement start angle at which the bubble 50 moves from the surface of the mask 25 is one of the indicators indicating the surface characteristics of the mask 25, and is used as an indication that the bubble 50 is likely to remain on the surface of the mask 25.

[0076] The angular difference $\Delta\varphi$ between the first contact angle φ_1 and the second contact angle φ_2 indicates asymmetry between the bubble 50 on the side of the movement direction and the side opposite to the movement direction. The smaller the asymmetry immediately before the start of movement, the more the bubble 50 is likely to move, and the larger the asymmetry, the less the bubble 50 is likely to move. That is, the larger the angular difference $\Delta\varphi$, which is the difference between the first contact angle φ_1 and the second contact angle φ_2 , the more the bubble 50 is likely to remain on the surface of the mask 25, and the smaller the angular difference $\Delta\varphi$, the less the bubble 50 is likely to remain on the surface of the mask 25. In a case where the angular difference $\Delta\varphi$ is equal to or less than 30° , the attachability of the bubble 50 to the surface of the mask 25 is weak. Therefore, the bubble 50 is likely to move. As the size of the bubble 50 is smaller, the buoyancy is smaller. Therefore, the bubble 50 tends to be less likely to move. According to the study by the inventors of the present disclosure, regarding the surface in which the angular difference of the bubble of 3 μL is equal to or less than 30° , there is the following effect. Even a minute bubble 50 having a diameter of several tens of μm or less is likely to move, and attachment of the minute bubble to the surface of the mask is suppressed.

[0077] Further, although the angular difference of the bubble 50 immediately before the bubble 50 starts moving from the surface of the mask 25 in water is defined herein, there is a correlation between the angular difference in water and the angular difference in the electrolytic solution during electroforming. That is, in a case where the angular difference in water is large, the angular difference in the electrolytic solution is large, and in a case where the angular difference in water is large, the angular difference in the electrolytic solution is also large. According to the study by the inventors of the present disclosure, there is the following effect. In a case where the angular difference immediately before the start of movement of the bubble of 3 μL on the surface of the mask 25 in water is equal to or less than 30° , it is possible to suppress remaining of the bubble and attachment of the minute bubble having a diameter of several tens of μm or less on the surface of the same mask 25 in the electrolytic solution during electroforming.

[0078] In a case where the bubble is not attached to the mask 25, the molding defect of the nozzle is suppressed. As described above, as the substrate 20 on which the non-conductive mask 25 is formed, the substrate 20 having the following configuration is used. In a case where a posture in which the surface of the mask 25 is vertically downward and is horizontal is set as a reference posture in a state where the substrate 20 is immersed in water, the angular difference $\Delta\varphi$ between the first contact angle φ_1 and the second contact angle φ_2 of the bubble 50 immediately before the bubble 50 of 3 μL attached to the surface of the mask 25 starts moving by tilting the surface of the mask 25 from the reference posture is equal to or less than 30° . Since such a substrate 20 is used, bubbles can be easily removed from the surface of the mask 25 as compared with the conventional case. Therefore, it is possible to reduce molding defects of the openings of the metal molded product. In particular, since it is easy to remove even minute bubble having a diameter of several tens of μm or less, there is a high effect of suppressing molding defects of the openings in the metal molded product having openings of 100 μm or less, such as the nozzle plate.

[0079] In a case where the respective angular differences $\Delta\varphi$ of the surface of the mask 25 and the conductive surface 20a are compared under the same condition, it is preferable to use the substrate 20 in which the angular difference $\Delta\varphi$ of the surface of the mask 25 is smaller.

[0080] By making the angular difference of the surface of the mask 25 smaller than that of the conductive surface 20a, as compared with a case where the angular differences $\Delta\varphi$ of the surface of the mask 25 and the conductive surface 20a are the same, the bubble 50 is likely to move from the surface of the mask 25 toward the conductive surface 20a. Therefore, it is possible to more reliably reduce molding defect of the opening.

[0081] As described above, in the first embodiment, as the substrate 20, the substrate 20 in which the movement start

angle θ of the bubble 50 on the surface of the mask 25 is equal to or less than 20° is used as the surface characteristic of the mask 25. Further, as described above, the second embodiment is an embodiment which uses the substrate 20 of which the angular difference $\Delta\phi$ which is a difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 of the bubble on the surface of the mask 25 as the surface characteristic of the mask 25 is equal to or less than 30° . Furthermore, as the substrate 20 on which the non-conductive mask 25 is formed, it is preferable to use the substrate 20 having the surface characteristics of each of the masks 25 of the first and second embodiments. That is, the posture of the surface of the mask 25 is vertically downward and horizontal is set as the reference posture in a state where the substrate 20 is immersed in water, and the surface of the mask 25 is tilted from the reference posture. In such a case, it is preferable to use the substrate 20 having the following configuration. The movement start angle is equal to or less than 20° , which is a tilt angle with respect to the reference posture of the surface of the mask 25 in a case where the bubble of 3 microliters (μL) attached to the surface of the mask 25 starts moving along the surface of the mask 25 due to buoyancy. In addition, regarding the contact angle of the bubble immediately before the bubble of 3 μL attached to the surface of the mask 25 in the reference posture starts moving by tilting the surface of the mask 25 from the reference posture, assuming that the contact angle on the side of the movement direction in which the bubble moves due to the buoyancy is the first contact angle and the contact angle on the side opposite to the movement direction is the second contact angle, the angular difference is 30° , which is a difference between the first contact angle and the second contact angle. By using such the substrate 20, it is possible to more effectively suppress attachment of the bubble on the mask 25, and thus it is possible to more effectively suppress the molding defect of the nozzle 12.

[0082] In each embodiment, it is preferable to use a substrate in which the contact angle ϕ of the bubble 50 attached to the mask 25 in the reference posture is equal to or greater than 130° . It is more preferable that the contact angle ϕ of the bubble attached to the mask 25 in the reference posture is equal to or greater than 130° .

[0083] The larger the contact angle of the bubble 50, the more the bubble on the surface of the mask 25 is likely to move, and the smaller the contact angle of the bubble 50, the more the bubble is likely to remain on the surface of the mask 25. In a case where the contact angle ϕ of the bubble 50 is equal to or greater than 130° , the attachment force of the bubble 50 to the surface of the mask 25 is weak. Therefore, the bubble 50 is likely to move. According to the study by the inventors of the present disclosure, regarding the surface in which the contact angle ϕ of the bubble 50 is equal to or greater than 130° , the following effect is further improved. Even a minute bubble 50 having a diameter of several tens of μm or less is likely to move, and attachment of the minute bubble 50 to the surface of the mask 25 is suppressed. Further, although the contact angle of the bubble 50 in water is defined herein, there is a correlation between the contact angle of the bubble 50 in water and the contact angle of the bubble 50 in the electrolytic solution during electroforming. That is, in a case where the contact angles of the bubbles in water are large, the contact angles of the bubbles in the electrolytic solution are also large, and in a case where the contact angles of the bubbles in water are large, the contact angles of the bubbles in the electrolytic solution are also large. According to the study by the inventors of the present disclosure, in a case where the contact angle of the bubble 50 of 3 μL attached to the mask 25 in the reference posture is equal to or greater than 130° , it is possible to suppress the remaining of the bubble 50 on the surface of the same mask 25 in the electrolytic solution during electroforming. As a result, there is an effect of suppressing attachment of the minute bubble having a diameter of several tens of μm or less.

[0084] In a case where the bubble 50 is not attached to the mask 25, the molding defect of the nozzle 12 can be suppressed. In the first or second embodiment, as the substrate 20 on which the non-conductive mask 25 is formed, the substrate 20 in which the contact angle ϕ of the bubble 50 attached to the mask 25 in the reference posture is equal to or greater than 130° is used. Thereby, since the bubble 50 is further easily removed from the surface of the mask, it is possible to further reduce molding defects of openings of the metal molded product. In particular, since it is easy to remove even the minute bubble 50 having a diameter of several tens of μm or less, the effect of suppressing the molding defect of the opening is further enhanced in the metal molded product having an opening of 100 μm or less, such as the nozzle plate 10.

[0085] In a case where the surface of the mask 25 is hydrophilic, the contact angle of the bubble 50 with respect to the surface of the mask 25 in water is large. Further, in a case where the surface of the mask 25 is hydrophobic, the contact angle of the bubble 50 with respect to the mask surface in water is small. That is, the more hydrophilic the surface of the mask 25 is, the larger the contact angle of the bubble 50 is, and the higher the effect of suppressing the attachment of the bubble 50 is.

[0086] Regarding the respective contact angles ϕ of the bubble 50 on the surface of the mask 25 and the conductive surface 20a of the substrate 20, in a case where the contact angles thereof in the reference posture are compared under the same condition, it is preferable to use the substrate 20 of which the contact angle ϕ is larger on the surface of the mask 25.

[0087] By making the contact angle ϕ of the bubble 50 on the surface of the mask 25 smaller than that of the conductive surface 20a, as compared with a case where the contact angles ϕ of the surface of the mask 25 and the conductive surface 20a are the same, the bubble 50 is likely to move from the surface of the mask 25 toward the conductive surface 20a. Therefore, it is possible to more reliably reduce molding defects of openings in the metal molded product.

[0088] In a case where the electroforming apparatus 30 shown in Fig. 5 described above is used, the substrate 20 is disposed in the electrolytic solution in a posture in which the conductive surface 20a is vertically downward. However, the substrate 20 may be disposed in a posture in which the conductive surface 20a is vertically upward. In a case where the conductive surface 20a is vertically upward, the bubble 50 is not pressed by the substrate 20. Therefore, the bubble 50 is likely to move due to buoyancy as compared with a case where the conductive surface 20a is vertically downward. Therefore, bubbles on the surface of the mask can be reduced more reliably. On the other hand, in a case where the conductive surface 20a is disposed to be vertically downward, a pressing force is applied by the substrate 20 to the bubble 50. Therefore, the bubble 50 is less likely to move as compared with a case where the conductive surface 20a is vertically upward. However, by using the substrate 20 described in the above-mentioned embodiment, even in a case where the conductive surface 20a is disposed to be vertically downward, attachment of a bubble to the surface of the mask 25 can be suppressed. As a result, it is possible to reduce molding defects of openings in the metal molded product. Further, by setting the conductive surface 20a in the vertically downward posture, it is possible to suppress foreign matter in the electrolytic solution falling from above in the vertical direction from being attached to the conductive surface as compared with a case of the vertically upward posture.

[0089] In the vertically downward posture, it is preferable that the tilt angle of the conductive surface having the mask 25 with respect to the horizontal direction is equal to or less than 60°. Attachment of foreign matter onto the conductive surface can be more reliably suppressed.

[0090] In the electroforming step of the metal molded product manufacturing method according to the above-mentioned embodiment, the electroforming is performed while the substrate 20 is rotated about an axis extending in the normal direction from the center position in the plane of the conductive surface by using the electroforming apparatus shown in Fig. 5. However, the electroforming may be performed while the substrate 20 is held at a fixed position without rotating the substrate 20.

[0091] However, by performing the electroforming step while rotating the substrate 20, it is possible to form the metal layer under electroforming conditions which are identical over the entire region without making the electroforming conditions different at the positions of the substrate 20. In particular, as shown in Fig. 3, in a case where a plurality of nozzle plate formation regions A, B, and C are provided in one substrate 20, individual differences between metal molded products are suppressed, and it is possible to manufacture the equivalent metal molded products.

[0092] The electroforming step of the metal molded product manufacturing method according to the above-mentioned embodiment is performed while the electrolytic solution is flowed in a direction in which the fluid pressure of the electrolytic solution 34 is applied toward the conductive surface 20a of the substrate 20. However, the electroforming step may be performed without causing the flow. However, by performing the electroforming step while flowing the electrolytic solution in a direction in which the fluid pressure of the electrolytic solution is applied toward the conductive surface 20a, attachment of foreign matter onto the surface of the mask 25 and the conductive surface 20a can be suppressed. Further, an effect of removing the bubble 50 remaining on the surface of the mask 25 can also be obtained. By suppressing the attachment of foreign matter to the conductive surface 20a, it is possible to obtain the metal molded product in which defects are suppressed. Further, by attachment of foreign matter onto the surface of the mask 25 and removal of the bubble 50 from the surface of the mask 25, it is possible to obtain the metal molded product in which the opening defects are suppressed.

[0093] Next, the substrate 20 in which the non-conductive mask 25 is formed on a part of the conductive surface 20a will be described in detail.

[0094] As the substrate 20 which has the conductive surface 20a, for example, as described in the above-mentioned embodiment, the substrate 20 may have a configuration in which the metal film 22 is provided on one surface of the glass wafer 21. The substrate 20 can be obtained by forming the metal film 22 such as nickel or copper on the glass wafer 21 through sputtering, vacuum vapor deposition, or the like. Further, the metal substrate may be used as the substrate 20 having the conductive surface 20a. In a case of a metal substrate, it is not necessary to separately form the metal film by sputtering or the like.

[0095] The non-conductive material which is a material of the non-conductive mask 25 may be a metal oxide or a photosensitive resin.

[0096] In a case where the metal oxide is used as the non-conductive material, a vapor deposition mask having openings having a desired mask shape is disposed on the substrate 20 so as to face the conductive surface 20a of the substrate 20, and vacuum vapor deposition is performed. Thereby, it is possible to form the mask 25. Examples of the metal oxide include silicon oxide. In a case where the metal oxide is used as the mask 25, the mask 25 remains on the substrate side at the time of peeling the metal layer in the peeling step described in the metal molded product manufacturing method according to the above-mentioned embodiment. Therefore, the substrate in which the non-conductive mask 25 is formed on a part of the conductive surface can be repeatedly used a plurality of times.

[0097] It is preferable that the non-conductive mask 25 is subjected to the hydrophilic treatment before the electroforming step. By performing the hydrophilic treatment, the movement start angle θ can be set to be equal to or less than 20°, which is the tilt angle with respect to the reference posture of the surface of the mask 25 in a case where the bubble 50 of 3 μ L attached to the surface of the mask 25 starts moving along the surface of the mask 25 due to buoyancy.

Alternatively, by performing the hydrophilic treatment, the angular difference $\Delta\phi$ can be set to be equal to or less than 30° , which is a difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 of the bubble immediately before the bubble of $3\ \mu\text{L}$ starts moving by tilting the surface of the mask 25 from the reference posture. Further, the movement start angle θ , which is a tilt angle with respect to a reference posture of the surface of the mask 25 in a case where bubble 50 of $3\ \mu\text{L}$ attached to the surface of the mask 25 starts moving along the surface of the mask 25 due to buoyancy, is equal to or less than 20° . In addition, by performing the hydrophilic treatment, the angular difference $\Delta\phi$ can be set to be equal to or less than 30° , which is a difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 of the bubble 50 immediately before the bubble 50 of $3\ \mu\text{L}$ starts moving by tilting the surface of the mask 25 from the reference posture.

[0098] The method of the hydrophilic treatment is not particularly limited, but plasma treatment or ultraviolet ozone treatment is preferable. By using the plasma treatment or the ultraviolet ozone treatment, the hydrophilic treatment can be integrally and uniformly performed over the entire region of the substrate 20.

[0099] In a case where the photosensitive resin is used as a material of the mask 25, the metal molded product manufacturing method of each of the above-mentioned embodiments may include a mask forming step of forming the mask on the conductive surface 20a. An example mask forming step includes a photosensitive resin coating step, an exposure step, and a development step. Further, the hydrophilic treatment of the photosensitive resin is performed at any stage after the coating step. In particular, it is preferable to perform the hydrophilic treatment on the photosensitive resin after the coating step and before the development step.

[0100] The mask provision step in the above-mentioned embodiment includes a mask forming step. A specific example of the mask forming step will be described with reference to Fig. 13.

[0101] As shown in Fig. 13, in the present example, the coating step S11, the hydrophilic treatment S12, the exposure step S13, and the development step S14 are performed in this order. Consequently, the hydrophilic treatment is performed before the exposure step.

[0102] First, in the coating step S11, the photosensitive resin film 24 is applied and formed on the metal film 22 on the glass wafer 21, that is, the conductive surface 20a of the substrate 20.

[0103] Next, as the hydrophilic treatment S12, the hydrophilic treatment is performed on the entire surface of the photosensitive resin film 24. As the hydrophilic treatment, the plasma treatment or the ultraviolet ozone treatment is performed.

[0104] Thereafter, in the exposure step S13, a mask 26 for forming a pattern is disposed on the photosensitive resin film 24, and the photosensitive resin film 24 is exposed to the pattern.

[0105] Then, in the development step S14, the exposed photosensitive resin film 24 is developed to obtain the substrate 20 provided with the mask 25 on the conductive surface 20a.

[0106] In such a manner, the hydrophilic treatment is performed on the photosensitive resin film 24. Therefore, in a case where the surface of the mask 25 is tilted from the reference posture in a state where the substrate 20 is immersed in water, the movement start angle θ is equal to or less than 20° , which is a tilt angle with respect to the reference posture of the surface of the mask 25 in a case where the bubble 50 of $3\ \mu\text{L}$ attached to the surface of the mask 25 starts moving along the surface of the mask 25 due to buoyancy. Further, the hydrophilic treatment is performed on the surface of the photosensitive resin film 24, that is, the mask 25. Therefore, the posture of the surface of the mask 25 which is vertically downward and horizontal is set as the reference posture in a state where the substrate 20 is immersed in water. Regarding the contact angle of the bubble immediately before the bubble 50 of $3\ \mu\text{L}$ attached to the surface of the mask 25 in the reference posture starts moving by tilting the surface of the mask 25 from the reference posture, assuming that the contact angle on the side of the movement direction in which the bubble moves due to buoyancy is the first contact angle ϕ_1 and the contact angle on the side opposite to the movement direction is the second contact angle ϕ_2 , the angular difference $\Delta\phi$ is equal to or less than 30° , which is a difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 .

[0107] A specific example of the mask forming step will be described with reference to Fig. 14.

[0108] As shown in Fig. 13, in the present example, the coating step S21, the exposure step S22, the hydrophilic treatment S23, and the development step S24 are performed in this order. Consequently, the hydrophilic treatment is performed after the exposure step S22 and before the development step S24.

[0109] First, in the coating step S21, the photosensitive resin film 24 is uniformly coated on the metal film 22 on the glass wafer 21, that is, the conductive surface 20a of the substrate 20.

[0110] Thereafter, in the exposure step S22, the mask 26 for forming a pattern is disposed on the photosensitive resin film 24, and the photosensitive resin film 24 is exposed to the pattern.

[0111] Next, as the hydrophilic treatment S23, the hydrophilic treatment is performed on the entire surface of the photosensitive resin film 24. As the hydrophilic treatment, the plasma treatment or the ultraviolet ozone treatment is performed.

[0112] Then, in the development step S24, the exposed photosensitive resin film 24 is developed to obtain the substrate 20 provided with the mask 25 on the conductive surface 20a.

[0113] In the case of the present example as well, the hydrophilic treatment is performed on the photosensitive resin film 24. Therefore, in a case where the surface of the mask 25 is tilted from the reference posture in a state where the substrate 20 is immersed in water, the movement start angle is equal to or less than 20° , which is a tilt angle with respect to the reference posture of the surface of the mask 25 in a case where the bubble 50 of $3\ \mu\text{L}$ attached to the surface of the mask 25 starts moving along the surface of the mask 25 due to buoyancy. Further, the hydrophilic treatment is performed on the surface of the photosensitive resin film 24, that is, the mask 25. Therefore, the posture of the surface of the mask 25 which is vertically downward and horizontal is set as the reference posture in a state where the substrate 20 is immersed in water. Regarding the contact angle of the bubble 50 immediately before the bubble 50 of $3\ \mu\text{L}$ attached to the surface of the mask 25 in the reference posture starts moving by tilting the surface of the mask 25 from the reference posture, assuming that the contact angle on the side of the movement direction in which the bubble moves due to buoyancy is the first contact angle ϕ_1 and the contact angle on the side opposite to the movement direction is the second contact angle ϕ_2 , the angular difference $\Delta\phi$ is equal to or less than 30° , which is a difference between the first contact angle ϕ_1 and the second contact angle ϕ_2 .

[0114] In the above, the hydrophilic treatment is performed before the exposure step or after the exposure step and before the development step. However, the hydrophilic treatment may be performed before the exposure step, after the exposure step, before the development step, or after the development step. In any stage of the hydrophilic treatment, the surface of the mask 25 is made hydrophilic, and the above-mentioned effect can be obtained. However, by performing the hydrophilic treatment before the exposure step or after the exposure step and before the development step, it is possible to suppress a decrease in yield due to a phenomenon that the metal layer 11 is peeled off from the conductive surface during electroforming.

[0115] Here, the effect of the hydrophilic treatment will be described.

[0116] A coated photosensitive resin film, which was not subjected to exposure, development, or cleaning treatment after coating formation, a developed and cleaned photosensitive resin film, which was subjected to exposure, development, or cleaning treatment, and a Ni sputter film were provided. For the films, the water contact angle before and after the ultraviolet ozone treatment as the hydrophilic treatment was measured. The Ni sputter film is an example of the metal film forming the conductive surface of the substrate. A low-pressure mercury lamp (emission main wavelength $254\ \text{nm}$, and output $200\ \text{W}$) was used as the ultraviolet ozone treatment, and irradiation was performed for 20 minutes.

[0117] The water contact angle was measured by using a contact angle meter DMo-501 manufactured by Kyowa Interface Science Co., Ltd., and an average value at 10 points was taken. Table 1 shows the results thereof.

[Table 1]

	Before hydrophilic treatment	After hydrophilic treatment
	water contact angle ($^\circ$)	water contact angle ($^\circ$)
Coated photosensitive resin	83.1	17.8
Developed and cleaned photosensitive resin	80.3	17.8
Ni sputter film	26.7	31.5

[0118] As shown in Table 1, the photosensitive resin was hydrolyzed by the ultraviolet ozone treatment, and the water contact angle was significantly decreased. The effect on the ultraviolet ozone treatment did not change significantly before and after the development cleaning. On the other hand, the Ni-sputter film had no effect of hydrophilization by the ultraviolet ozone treatment, and the result thereof was that the water contact angle was slightly increased. Consequently, in the hydrophilic treatment, substantially the same hydrophilization effect was obtained even in a state where the exposure and development treatments were not performed.

[0119] The contact angle ϕ , the movement start angle θ , and the angular difference $\Delta\phi$ of the bubble 50 of $3\ \mu\text{L}$ in water were measured.

[0120] Fig. 15 shows the results of measuring the contact angle ϕ of bubble of $3\ \mu\text{L}$ in water for each of the Ni sputter film, the photosensitive resin film, and the photosensitive resin film subjected to the ultraviolet ozone treatment as the hydrophilic treatment. The contact angle was measured three times for each film. In the drawing, a range indicated by the bar is a range of a minimum value or more and a maximum value or less of the three-times measured values, and a dot indicates an average value of the three-times measured values. In the following description, the average value of the three-times measured values is set as the contact angle ϕ of each film.

[0121] The contact angle ϕ of the bubble with respect to the Ni sputter film was 125° , the contact angle ϕ of the bubble with respect to the photosensitive resin film not subjected to the hydrophilic treatment was 115° , and the contact angle ϕ of the bubble with respect to the photosensitive resin film subjected to the ultraviolet ozone treatment was 145° . The contact angle ϕ of the bubble with respect to the photosensitive resin film not subjected to the hydrophilic treatment is

less than that of the Ni sputter film. On the other hand, the contact angle ϕ of the bubble with respect to the photosensitive resin film subjected to the hydrophilic treatment is greater than the contact angle ϕ of the bubble with respect to the photosensitive resin film and the Ni sputter film not subjected to the hydrophilic treatment. Consequently, the effect of increasing the contact angle ϕ of the bubble was obtained by the hydrophilic treatment.

[0122] Further, the bubble movement start angle θ and the angular difference $\Delta\phi$ were also measured for each film. Fig. 16 shows the results of measuring the movement start angle θ of the bubble for each of the Ni sputter film, the photosensitive resin film, and the photosensitive resin film which is subjected to the ultraviolet ozone treatment as the hydrophilic treatment. The movement start angle was measured three times for each film. In the drawing, a range indicated by the bar is a range of a minimum value or more and a maximum value or less of the three-times measured values, and a dot indicates an average value of the three-times measured values. In the following description, the average value of the three-times measured values is set as the movement start angle θ of each film.

[0123] The movement start angle θ of the Ni sputter film was 38° , the movement start angle θ of the photosensitive resin film not subjected to the hydrophilic treatment was 48° , and the movement start angle θ of the photosensitive resin film subjected to the ultraviolet ozone treatment was substantially 0° . The movement start angle θ of the photosensitive resin film not subjected to the hydrophilic treatment was greater than that of the Ni sputter film, and the bubble did not move even in a case where tilted up to 60° in some cases. On the other hand, the movement start angle θ of the photosensitive resin which was subjected to the hydrophilic treatment was approximately 0° . In the photosensitive resin subjected to the hydrophilic treatment, bubbles were moving before the angle of the substrate was tilted, and a high effect of improving the mobility of the bubbles on the photosensitive resin film by performing the hydrophilic treatment was obtained.

[0124] Fig. 17 is a diagram schematically showing a shape of a bubble in each film during measurement of the angular difference. Fig. 17A shows a shape of a bubble on the Ni sputter film in a case of measuring the angular difference. Fig. 17B shows a shape of a bubble on the photosensitive resin film not subjected to the hydrophilic treatment in a case of measuring the angular difference. Fig. 17C shows a shape of a bubble on the photosensitive resin film subjected to the hydrophilic treatment in a case of measuring the angular difference.

[0125] The angular difference $\Delta\phi$ was 44° for the photosensitive resin film that had not been subjected to the hydrophilic treatment, 36° for the Ni sputter film, and approximately 0° for the photosensitive resin film that had been subjected to the hydrophilic treatment. The angular difference $\Delta\phi$ of the photosensitive resin film not subjected to the hydrophilic treatment is greater than that of the Ni sputter film. On the other hand, the angular difference $\Delta\phi$ of the photosensitive resin subjected to the hydrophilic treatment was approximately 0° , which was smaller than that of the photosensitive resin film and the Ni sputter film not subjected to the hydrophilic treatment. As described above, the effect of improving the mobility of a bubble on the photosensitive resin film by performing the hydrophilic treatment is also shown from the angular difference $\Delta\phi$.

[0126] According to the study by the present inventors, in a case where the oxygen plasma treatment is performed instead of the ultraviolet ozone treatment as the hydrophilic treatment, the same tendency as in the case of the ultraviolet ozone treatment is obtained as the effect of the hydrophilic treatment.

Examples

[0127] Hereinafter, Examples 1 and 2 and a comparative example will be described.

[Example 1]

[0128] A nozzle plate was manufactured through the metal molded product manufacturing method according to Example 1. The manufacturing method according to Example 1 was as follows.

[0129] The Ni film was sputter-deposited on the glass wafer to obtain a substrate made of the Ni film and having the conductive surface. Then, a mask for forming a nozzle was formed on the surface of the Ni film of the substrate by the following mask forming step to provide a substrate having three nozzle plate formation regions A, B, and C as shown in Fig. 3. The nozzle plate formation regions A, B, and C were $100\text{ mm} \times 40\text{ mm}$, and 130 masks having a diameter of $150\text{ }\mu\text{m}$ and a mask thickness of $2\text{ }\mu\text{m}$ were arranged in 8 rows.

[0130] First, a photosensitive resin film is applied and formed on the surface of the Ni film on the glass wafer (coating step), a mask for forming a pattern was disposed on the photosensitive resin film, and the photosensitive resin was exposed to the pattern (exposure step), and developed (development step) to form a mask. Then, the surface of the mask and the Ni film was subjected to the hydrophilic treatment with oxygen plasma.

[0131] For the obtained substrate, the water contact angle of the mask surface was 8.4° . The contact angle of the bubble on the mask surface in water was 148° , the movement start angle was 0° , and the angular difference between the first contact angle and the second contact angle was 0° .

[0132] A substrate having a non-conductive mask formed on a part of the conductive surface formed of the Ni film

obtained in the above steps was used, the electroforming apparatus described with reference to Fig. 5 was used, and the Ni electroforming is performed while the glass wafer is rotated in the electroforming tank. Thereby, a metal layer was grown on the Ni film of the substrate (electroforming step). The electroforming was performed until the thickness of the metal layer became approximately 50 μm and the opening diameter on the mask reached a desired value (design value 40 μm).

[0133] Thereafter, the metal layer was peeled from the substrate (peeling step), and in the peeling step, the mask attached to a part of the metal layer was removed (mask removing step) to provide the nozzle plate of Example 1 formed of the metal layer.

[Comparative Example]

[0134] A nozzle plate was manufactured through the metal molded product manufacturing method according to a comparative example.

[0135] In the manufacturing method according to the comparative example, in the manufacturing step of Example 1, the hydrophilic treatment was not performed in the mask forming step. A nozzle plate of the comparative example was provided in a similar manner as in Example 1 except for this point.

[0136] The water contact angle of the surface of the mask was 80.3° with respect to the substrate which was obtained in the mask forming step. The contact angle of the bubble on the surface of the mask in water was 110°, the movement start angle was 38°, and the angular difference between the first contact angle and the second contact angle was 40°.

[Example 2]

[0137] A nozzle plate was manufactured through the metal molded product manufacturing method according to Example 2.

[0138] In the manufacturing method according to Example 2, in the manufacturing step of Example 1, the hydrophilic treatment was performed in the mask forming step after the exposure step and before the development step. Further, the nozzle plate of Example 2 was provided in a similar manner as in Example 1 except that the design value of the nozzle diameter was set to 41 μm .

[0139] The water contact angle of the surface of the mask was 18° with respect to the substrate which was obtained in the mask forming step. The contact angle of the bubble on the mask surface in water was 145°, the movement start angle was 2°, and the angular difference between the first contact angle and the second contact angle was 5°.

[0140] The conditions of the mask surface of the substrate of Example 3 were substantially the same as those of Example 1.

[0141] The nozzle diameters of the nozzle plates obtained in each of the examples and the comparative example were measured.

[0142] In Examples 1 and the comparative example, the nozzle diameters of the nozzle plates 10A, 10B, and 10C respectively obtained in the nozzle plate formation regions A, B, and C were measured. In Example 2, the nozzle diameter of the nozzle plate 10A obtained in the nozzle plate formation region A was measured.

[0143] Fig. 18 shows measurement results for Example 1, Fig. 19 shows measurement results for the comparative example, and Fig. 20 shows measurement results for Example 2. Figs. 18A to 18H show measurement results for respective rows 1 to 8 in the sub-scanning direction of the nozzle plates 10A, 10B, and 10C of Example 1. Figs. 19A to 19H are measurement results for respective columns 1 to 8 in the sub-scanning direction of the nozzle plates 10A, 10B, and 10C of the comparative examples. Figs. 20A to 20H are measurement results for respective rows 1 to 8 in the sub-scanning direction of the nozzle plate 10A of Example 2. In each drawing, the vertical axis indicates the nozzle opening, and the unit is mm. Further, the horizontal axis indicates the nozzle position in the main scanning direction of the nozzle plate.

[0144] As shown in Fig. 19, in the nozzle plate of the comparative example, a plurality of nozzles having a significantly reduced diameter are present in any of the rows and regardless of the formation region. As described with reference to Figs. 7 to 10, it is considered that this phenomenon of decreasing the diameter is caused by the fact that the metal layer is formed by swelling and the nozzle is partially blocked. As shown in Fig. 18, in the nozzle plate of Example 1, the number of nozzles having a significantly smaller diameter is extremely small as compared with the comparative example. Further, as shown in Fig. 20, in Example 2, as in Example 1, the number of nozzles having a significantly smaller diameter is extremely small as compared with the comparative example.

[0145] That is, it is clear that the manufacturing methods of Examples 1 and 2 have the effect of suppressing molding defects of the openings in the case of manufacturing the metal molded product having the openings by electroforming.

[0146] The disclosure of JP2020-113520A filed on June 30, 2020 is incorporated herein by reference in its entirety.

[0147] All documents, patent applications, and technical standards described in the present specification are incorporated into the present specification by reference to the same extent as in a case where the individual documents,

patent applications, and technical standards were specifically and individually stated to be incorporated by reference.

Claims

1. A metal molded product manufacturing method comprising:

an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step,

wherein in a case where a posture of a surface of the mask which is vertically downward and horizontal is set as a reference posture in a state where the substrate is immersed in water and the surface of the mask is tilted from the reference posture, a movement start angle, which is a tilt angle of the surface of the mask with respect to the reference posture in a case where a bubble of 3 μL attached to the surface of the mask in the reference posture starts moving along the surface of the mask due to buoyancy, is equal to or less than 20° .

2. The metal molded product manufacturing method according to claim 1,

wherein in a case where the respective movement start angles of the surface of the mask and the conductive surface are compared under the same condition, the movement start angle of the surface of the mask is smaller.

3. The metal molded product manufacturing method according to claim 1 or 2,

wherein regarding a contact angle of the bubble attached to the surface of the mask in the reference posture immediately before the bubble starts moving by tilting the surface of the mask from the reference posture, assuming that the contact angle on a side in a movement direction in which the bubble moves due to buoyancy is a first contact angle and the contact angle on a side opposite to the movement direction is a second contact angle, an angular difference, which is a difference between the first contact angle and the second contact angle, is equal to or less than 30° .

4. A metal molded product manufacturing method comprising:

an electroforming step of growing a metal layer on a conductive surface through a metal precipitated from an electrolytic solution in a state where a substrate having a non-conductive mask formed on a part of the conductive surface is used and the substrate is immersed in the electrolytic solution and forming an opening at a position corresponding to the mask so as to manufacture a metal molded product having an opening by performing the electroforming step,

wherein in a case where a posture of a surface of the mask which is vertically downward and horizontal is set as a reference posture in a state where the substrate is immersed in water, regarding a contact angle of the bubble of 3 μL attached to the surface of the mask in the reference posture immediately before the bubble starts moving by tilting the surface of the mask from the reference posture, assuming that the contact angle on a side in a movement direction in which the bubble moves due to buoyancy is a first contact angle and the contact angle on a side opposite to the movement direction is a second contact angle, an angular difference, which is a difference between the first contact angle and the second contact angle, is equal to or less than 30° .

5. The metal molded product manufacturing method according to claim 3 or 4,

wherein in a case where the respective angular differences of the surface of the mask and the conductive surface are compared under the same condition, the angular difference of the surface of the mask is smaller.

6. The metal molded product manufacturing method according to any one of claims 1 to 5,

wherein a contact angle of the bubble attached to the mask in the reference posture is equal to or greater than 130° .

7. The metal molded product manufacturing method according to claim 6,

wherein in a case where the respective contact angles of the surface of the mask and the conductive surface in the reference posture are compared under the same condition, the contact angle of the surface of the mask is greater.

8. The metal molded product manufacturing method according to any one of claims 1 to 7,

wherein a hydrophilic treatment is performed on the mask before the electroforming step.

9. The metal molded product manufacturing method according to claim 8,
wherein the hydrophilic treatment is a plasma treatment or an ultraviolet ozone treatment.
- 5 10. The metal molded product manufacturing method according to any one of claims 1 to 9, wherein a non-conductive material which is a material of the mask is a metal oxide.
11. The metal molded product manufacturing method according to any one of claims 1 to 9,
wherein a non-conductive material which is a material of the mask is a photosensitive resin.
- 10 12. The metal molded product manufacturing method according to claim 11, further comprising a mask forming step of forming a mask on the conductive surface,

wherein the mask forming step includes a coating step of uniformly coating the conductive surface with the
15 photosensitive resin, an exposure step of exposing the photosensitive resin in accordance with a pattern of the mask, and a development step of developing the photosensitive resin which is exposed, and
a hydrophilic treatment is performed on the photosensitive resin before the development step.
13. The metal molded product manufacturing method according to claim 12,
wherein the hydrophilic treatment is performed after the exposure step.
- 20 14. The metal molded product manufacturing method according to claim 12,
wherein the hydrophilic treatment is performed before the exposure step.
- 15 15. The metal molded product manufacturing method according to any one of claims 1 to 14,
wherein in the electroforming step, the substrate is disposed in the electrolytic solution in a posture in which the
25 conductive surface having the mask is vertically downward.
16. The metal molded product manufacturing method according to claim 15,
wherein in the posture in which the conductive surface is vertically downward, a tilt angle of the conductive surface
30 having the mask with respect to the horizontal direction is equal to or less than 60°.
17. The metal molded product manufacturing method according to any one of claims 1 to 16,
wherein the electroforming step is performed while the substrate is rotated around an axis extending in a normal
35 direction from a center position in a plane of the conductive surface.
18. The metal molded product manufacturing method according to any one of claims 1 to 17,
wherein the electroforming step is performed while the electrolytic solution is flowed in a direction in which a fluid
40 pressure of the electrolytic solution is applied toward the conductive surface having the mask.
19. The metal molded product manufacturing method according to any one of claims 1 to 18,
wherein the metal molded product is a nozzle plate used for a printing head of an inkjet printer.

FIG. 1

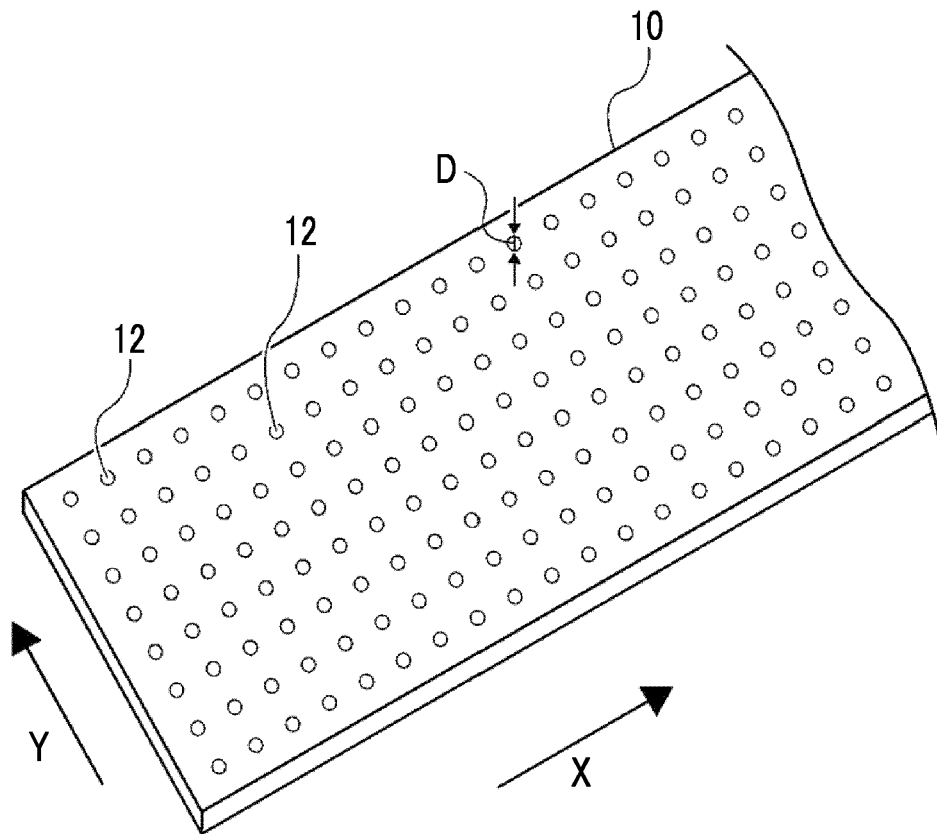


FIG. 2

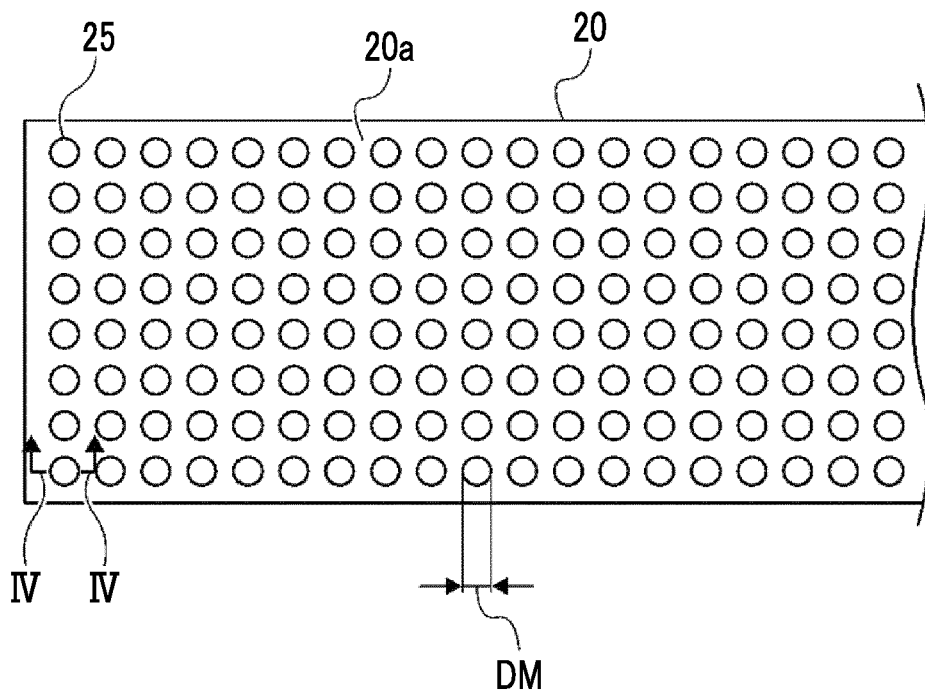
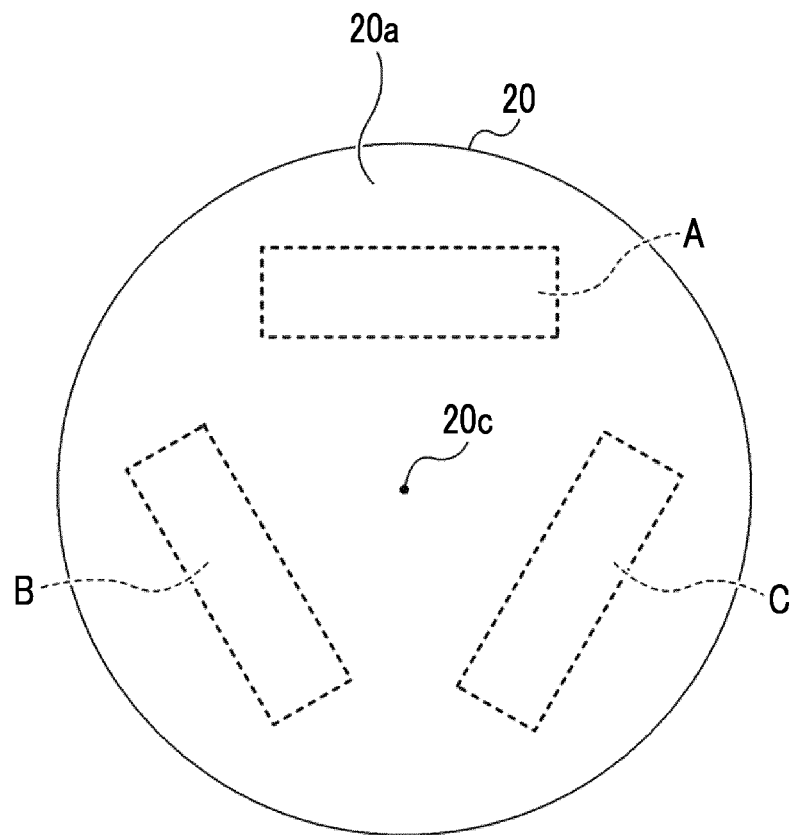


FIG. 3



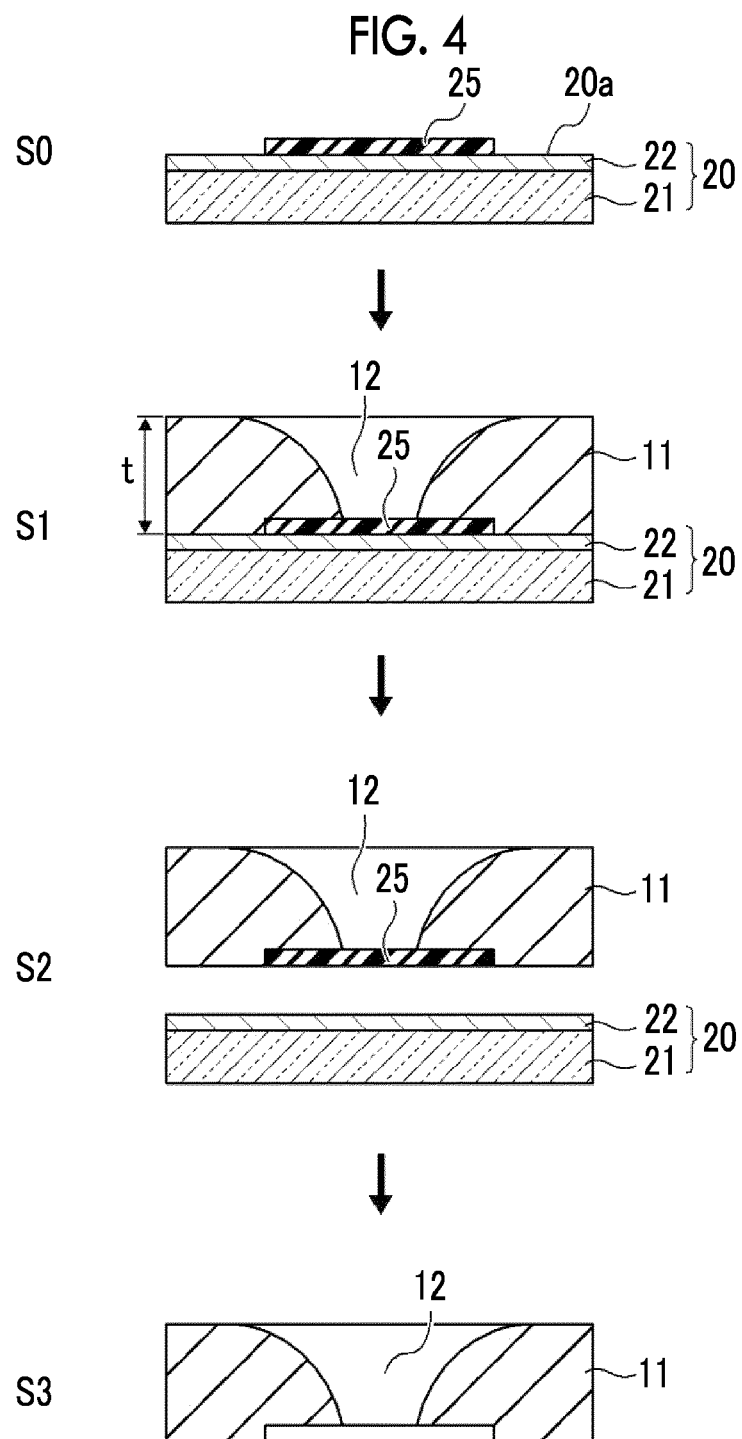


FIG. 5

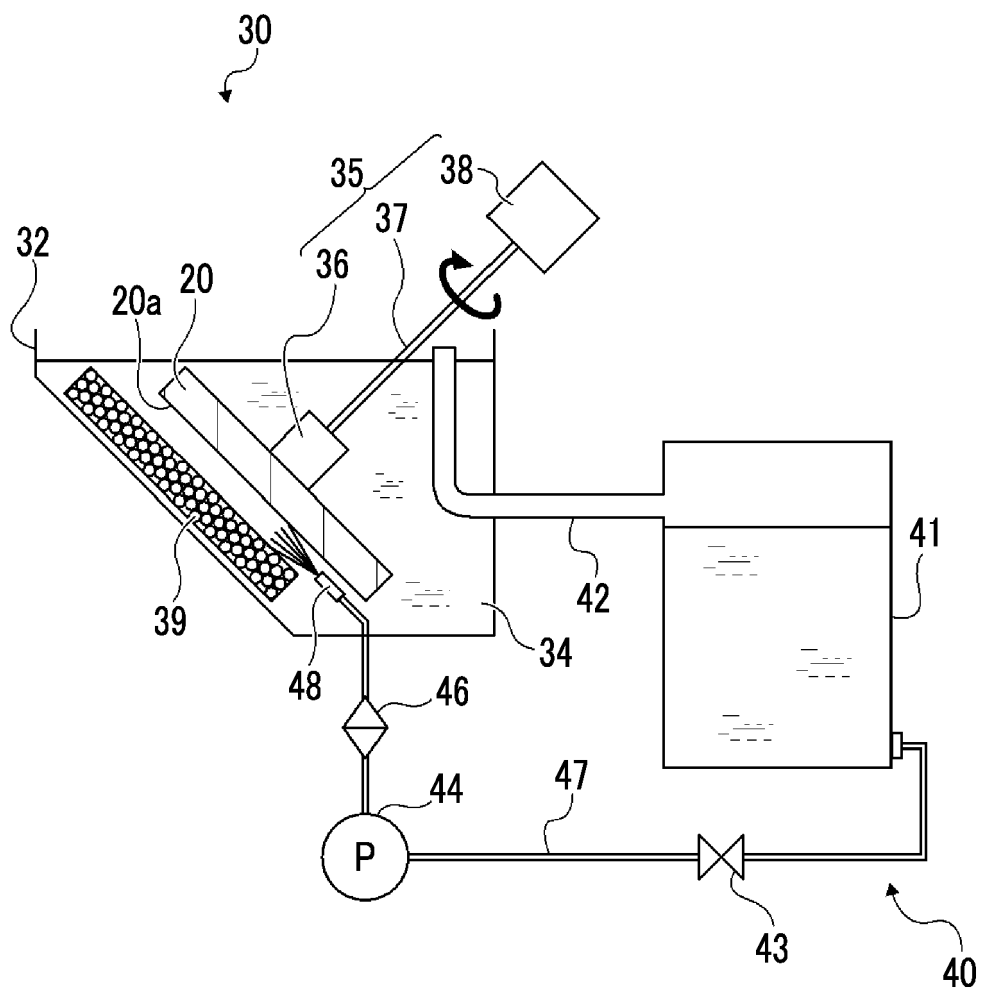


FIG. 6

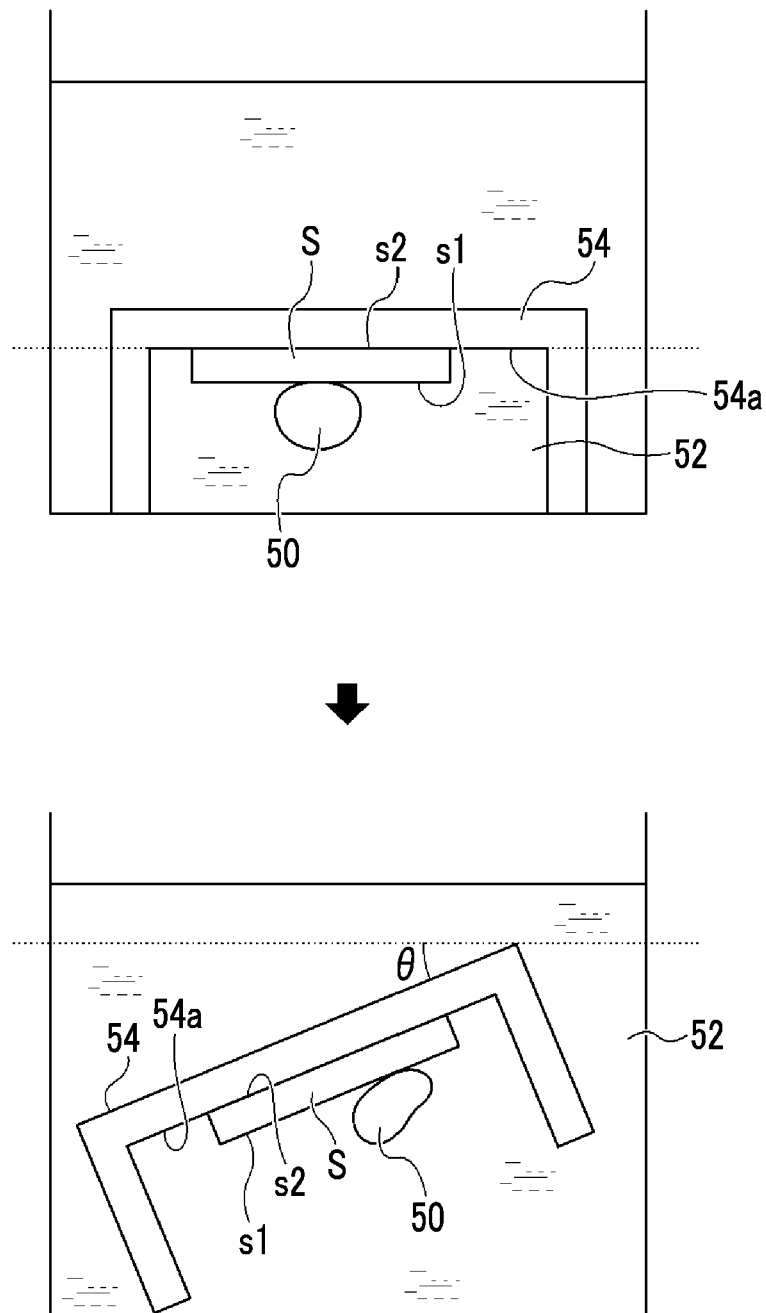


FIG. 7

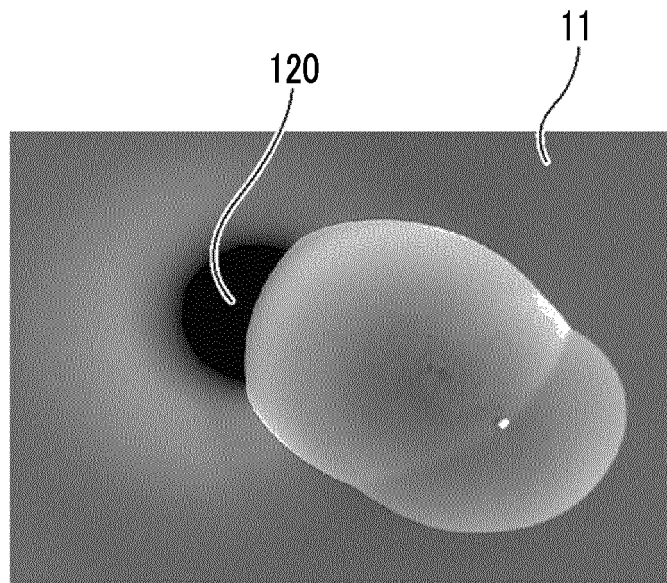


FIG. 8

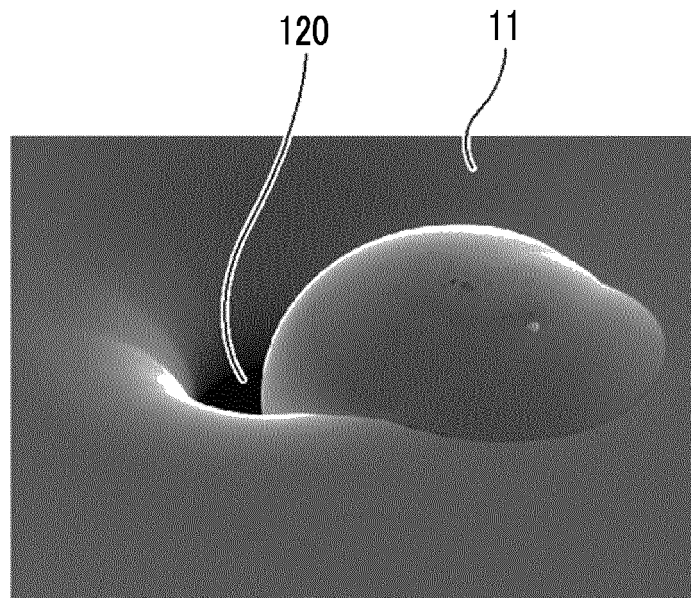


FIG. 9

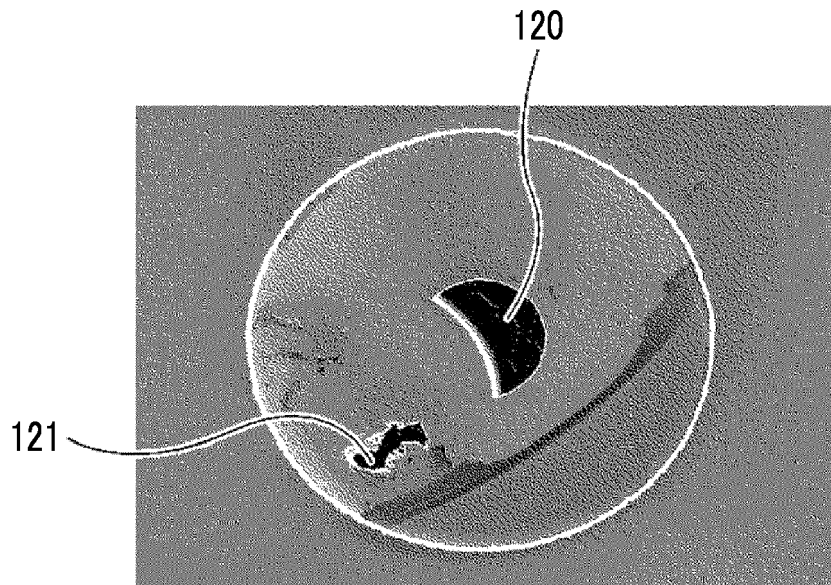


FIG. 10

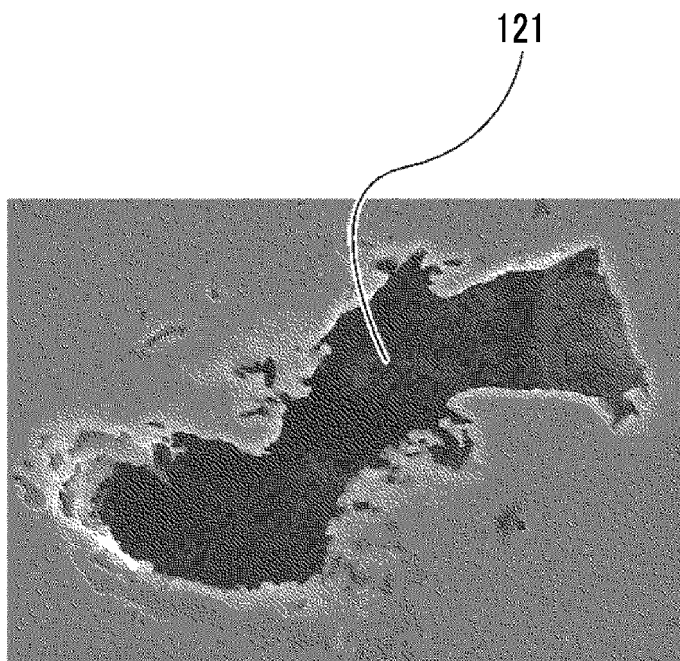


FIG. 11

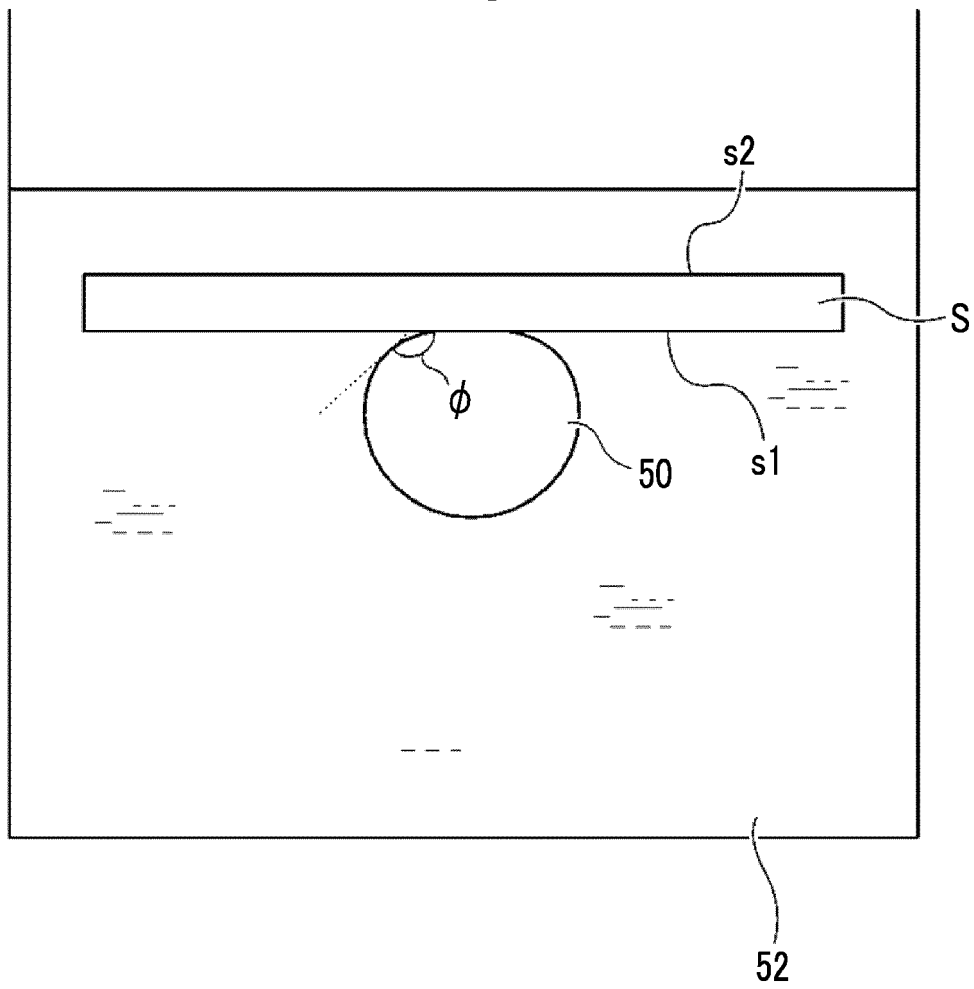


FIG. 12

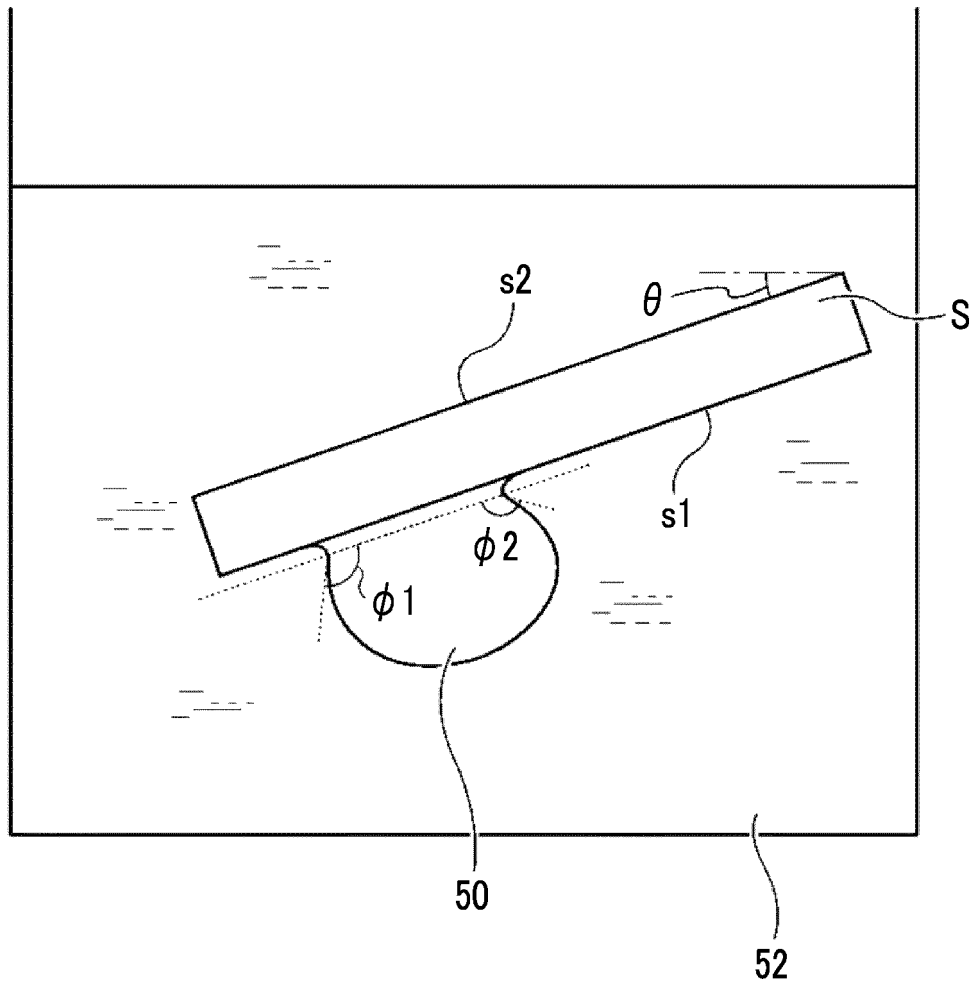


FIG. 13

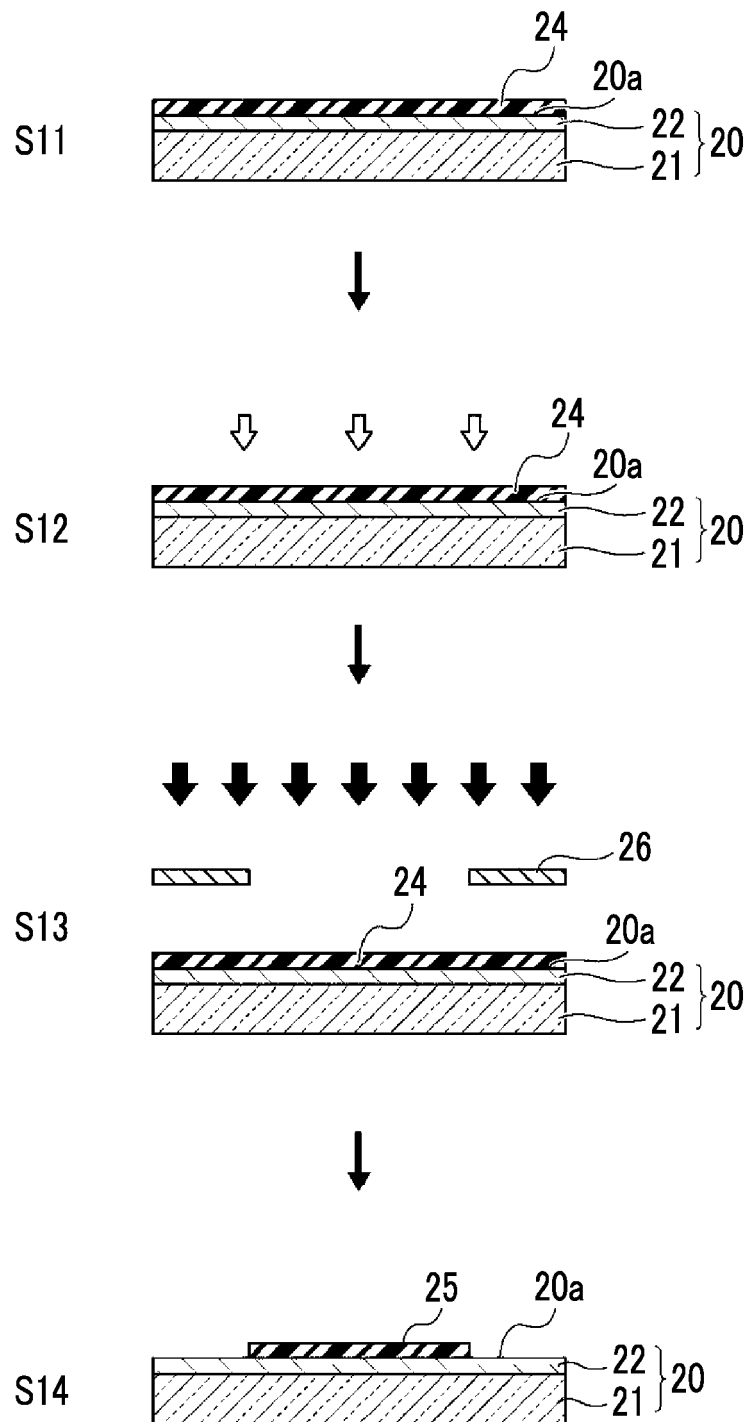


FIG. 14

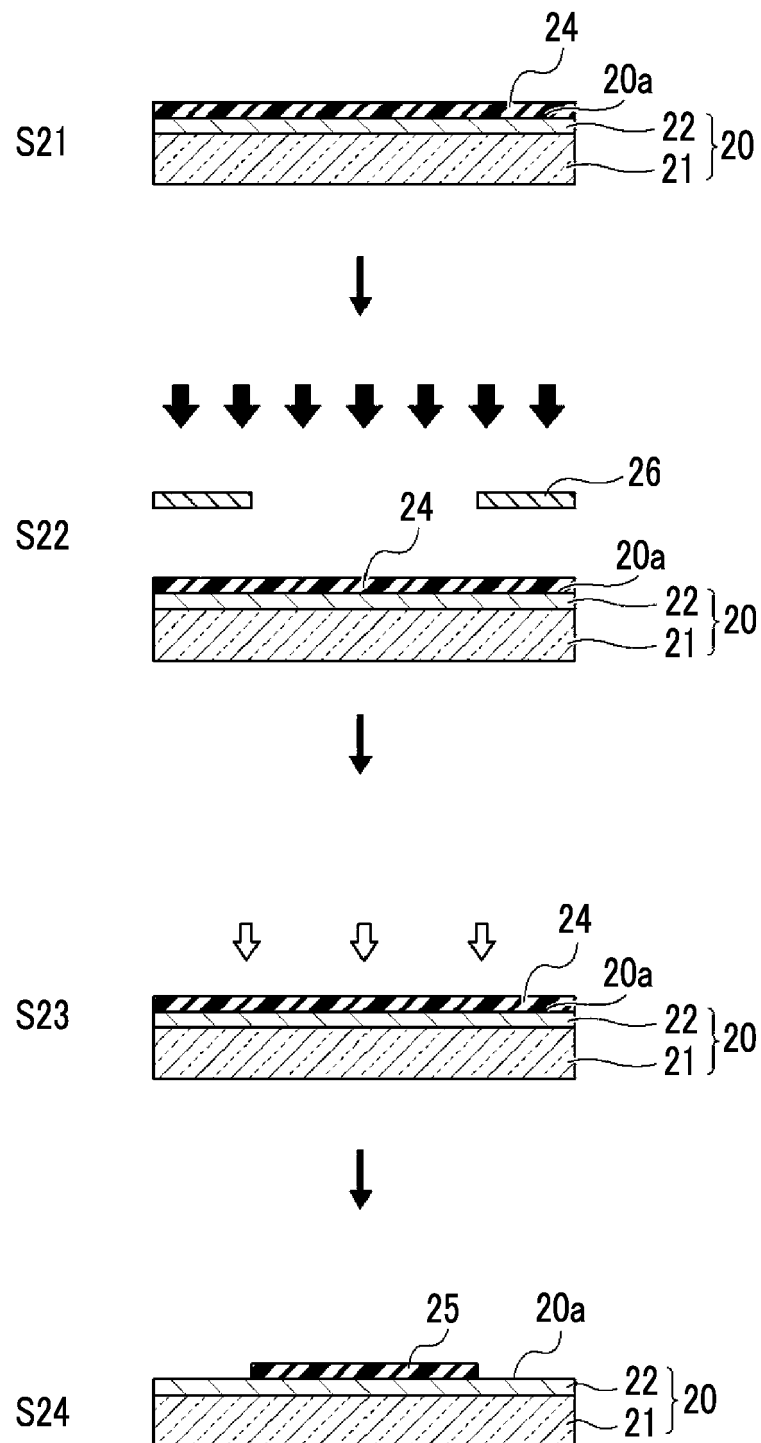


FIG. 15

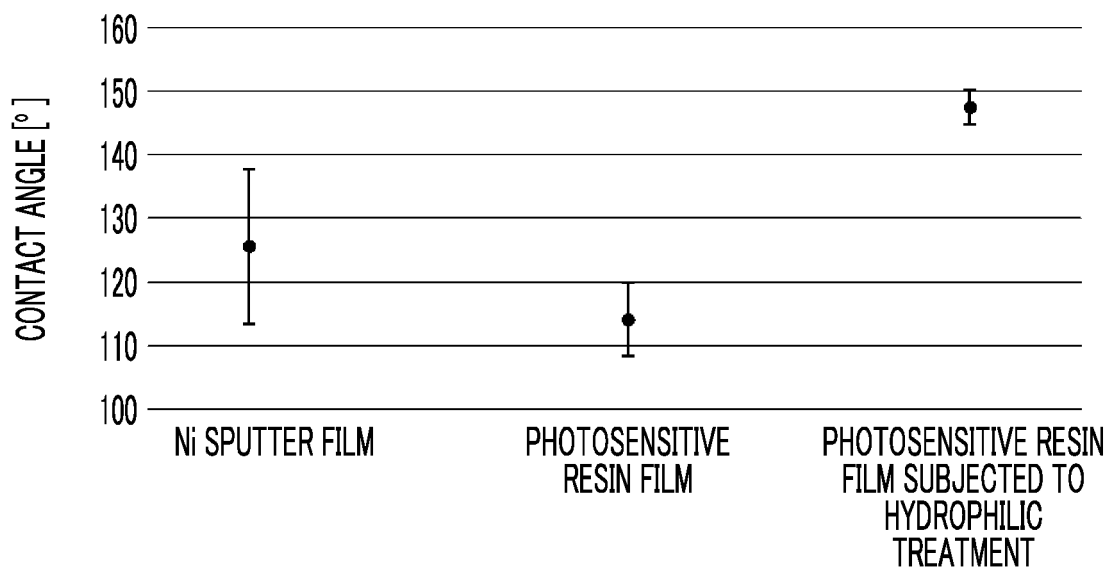


FIG. 16

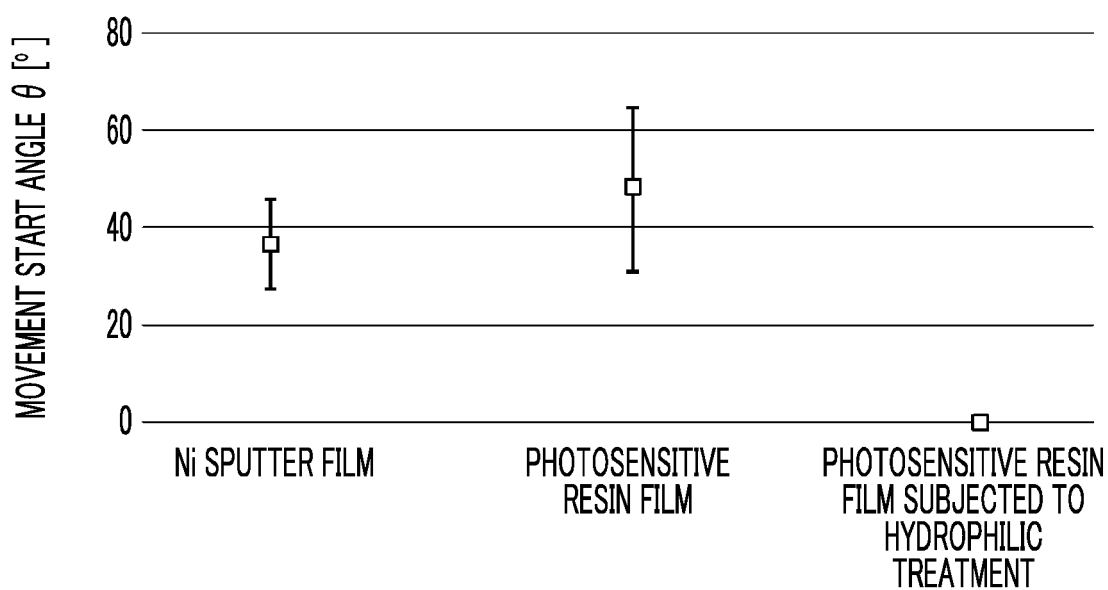


FIG. 17A

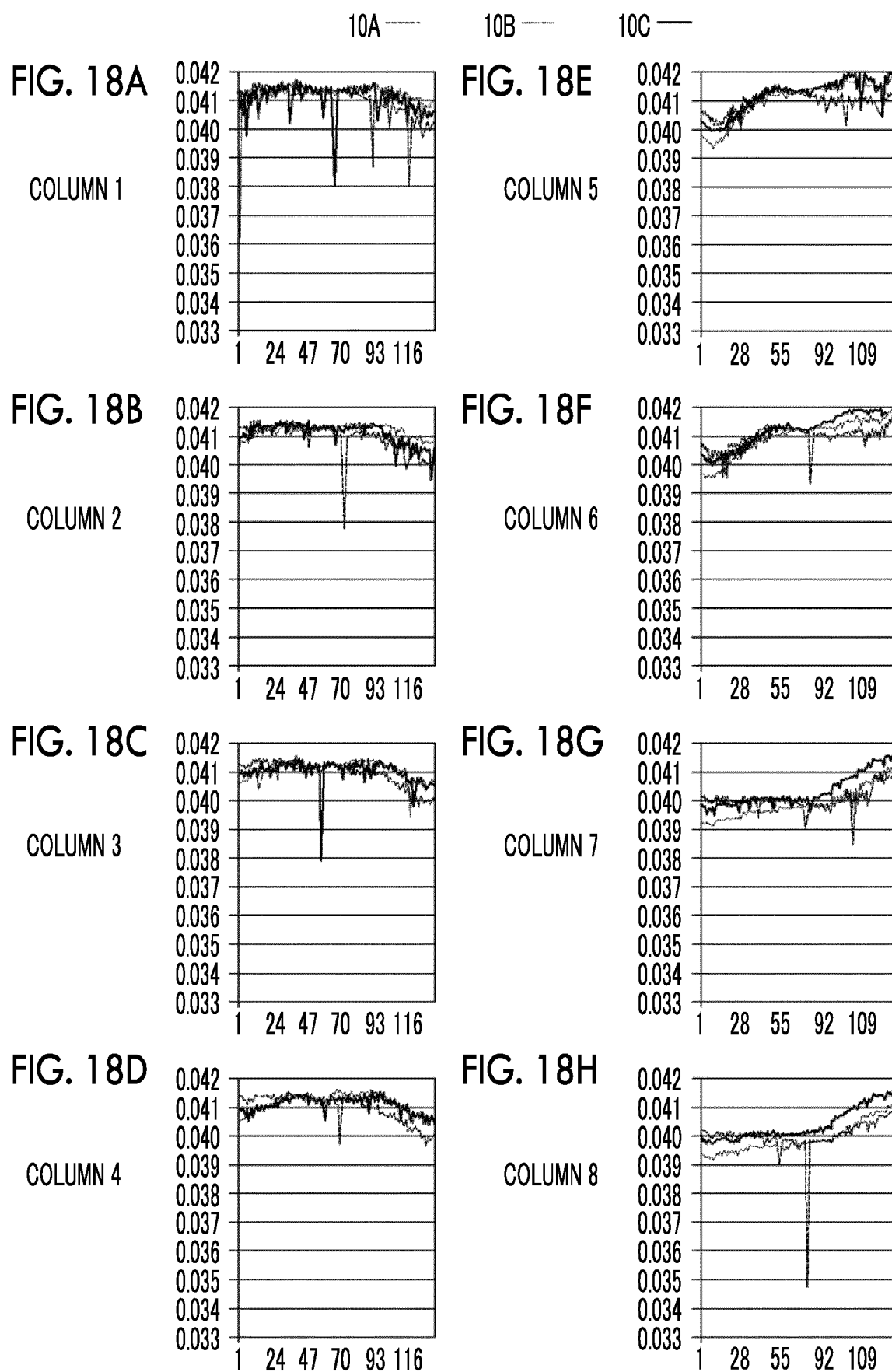


FIG. 17B



FIG. 17C





10A ---- 10B — 10C —

FIG. 19A

COLUMN 1

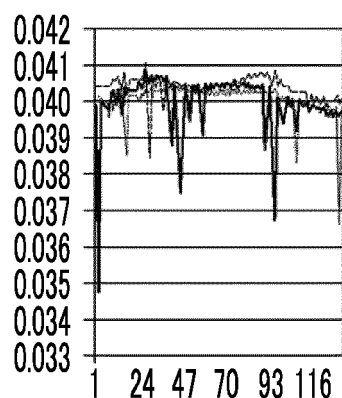


FIG. 19E

COLUMN 5

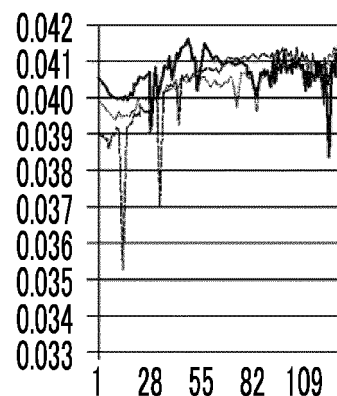


FIG. 19B

COLUMN 2

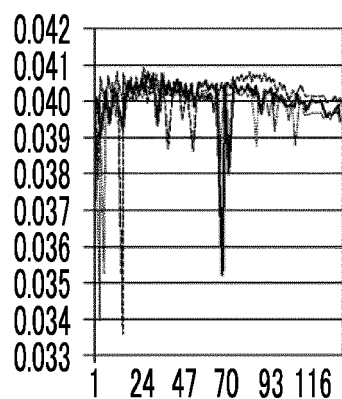


FIG. 19F

COLUMN 6

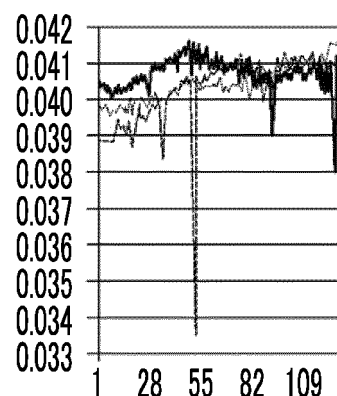


FIG. 19C

COLUMN 3

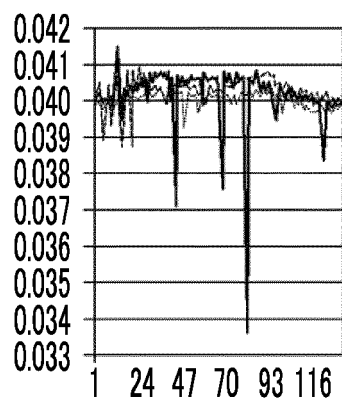


FIG. 19G

COLUMN 7

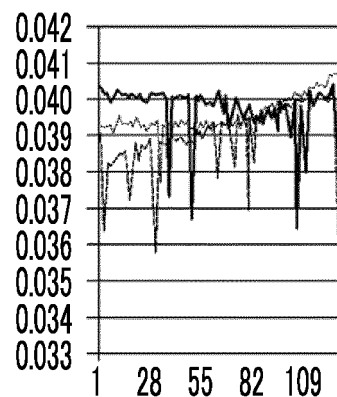


FIG. 19D

COLUMN 4

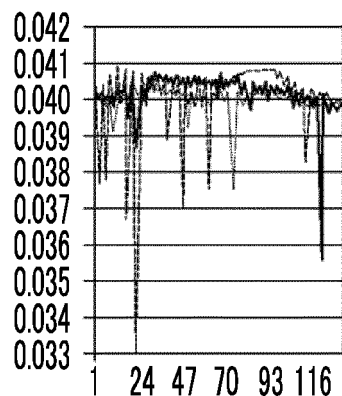
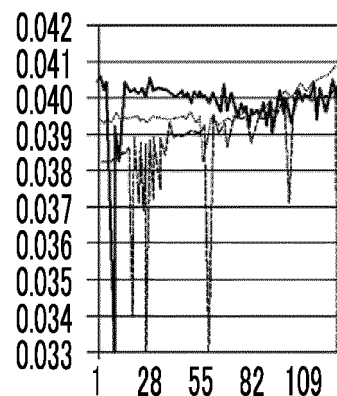


FIG. 19H

COLUMN 8



10A -----

FIG. 20A

COLUMN 1

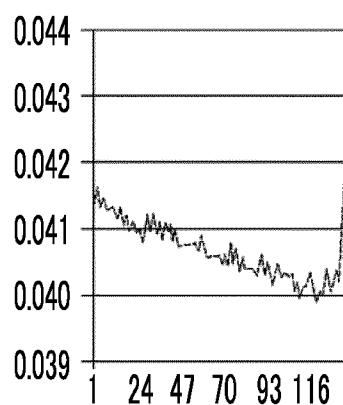


FIG. 20E

COLUMN 5

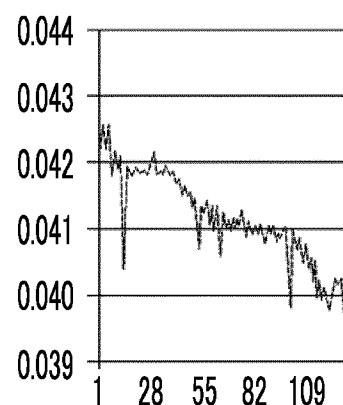


FIG. 20B

COLUMN 2

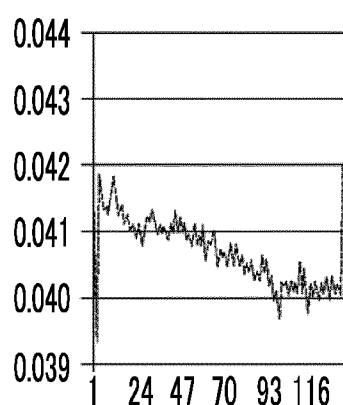


FIG. 20F

COLUMN 6

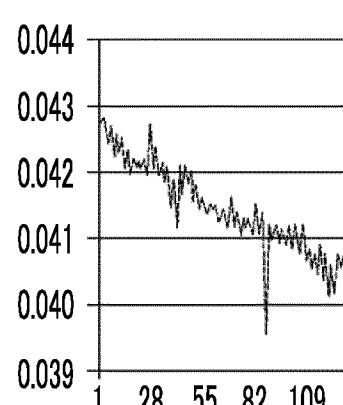


FIG. 20C

COLUMN 3

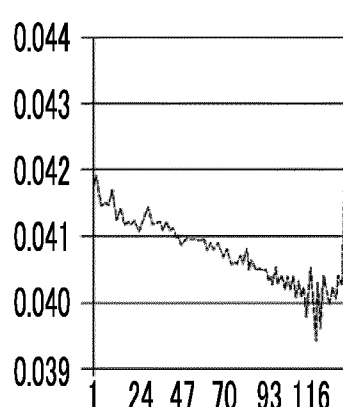


FIG. 20G

COLUMN 7

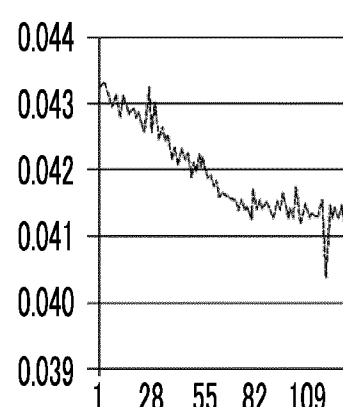


FIG. 20D

COLUMN 4

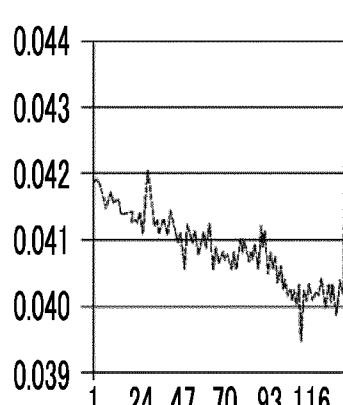
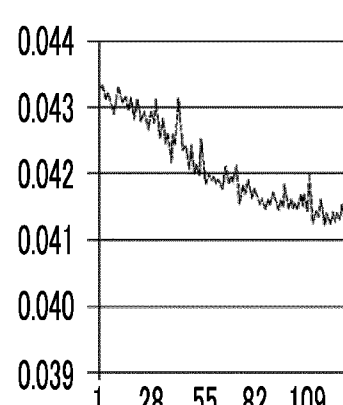


FIG. 20H

COLUMN 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/024216

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C25D1/00(2006.01)i, C25D1/08(2006.01)i, C25D21/04(2006.01)i,
C25D21/10(2006.01)i, B41J2/16(2006.01)i

FI: C25D1/00381, B41J2/16505, C25D1/08311, C25D21/10301, C25D21/04

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)

Int.Cl. C25D1/00, C25D1/08, C25D21/04, C25D21/10, B41J2/16

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2021

Registered utility model specifications of Japan 1996-2021

Published registered utility model applications of Japan 1994-2021

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-77433 A (ALPS ELECTRIC CO., LTD.) 14 April 2011 (2011-04-14), claims, paragraphs [0034], [0040]-[0051], [0061], fig. 1, 5	1-9, 11, 18
A	JP 2002-172789 A (KONICA CORPORATION) 18 June 2002 (2002-06-18), claims, paragraphs [0030]-[0035]	1-19
A	JP 7-6414 A (CANON INC.) 10 January 1995 (1995-01-10), claims, paragraphs [0011]-[0017], fig. 1	1-19
A	JP 9-106081 A (DAI NIPPON PRINTING CO., LTD.) 22 April 1997 (1997-04-22), entire text	1-19
A	JP 11-295903 A (TOKYO ELECTRON LTD.) 29 October 1999 (1999-10-29), entire text	1-19
A	JP 2008-23792 A (FUJIFILM CORPORATION) 07 February 2008 (2008-02-07), entire text	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

14 July 2021

Date of mailing of the international search report

27 July 2021

Name and mailing address of the ISA/

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku,

Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2021/024216

5	JP 2011-77433 A	14 April 2011	(Family: none)
	JP 2002-172789 A	18 June 2002	(Family: none)
	JP 7-6414 A	10 January 1995	(Family: none)
10	JP 9-106081 A	22 April 1997	(Family: none)
	JP 11-295903 A	29 October 1999	(Family: none)
15	JP 2008-23792 A	07 February 2008	(Family: none)

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Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2008023792 A [0002] [0003] [0004] [0006] [0007]
- JP 2002080995 A [0005] [0009]
- JP 2020113520 A [0146]