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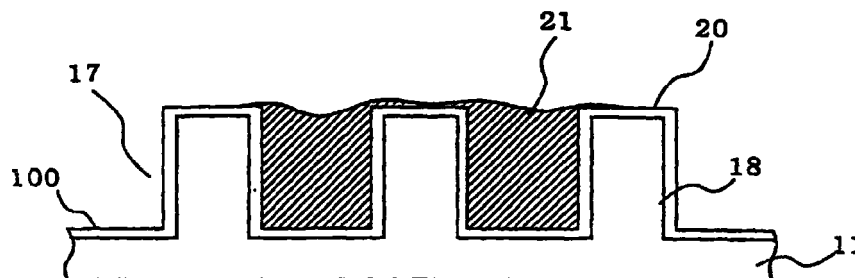
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(54) **HYDROPHILIC STRUCTURE, INK-JET PRINTING HEAD, METHOD OF THEIR PRODUCTION, INK-JET PRINTER, AND OTHER STRUCTURAL MEMBERS**

(57) A structure in which the hydrophilic properties are retained for long period of time, an ink-jet printing head having this structure, a method of their production, an ink-jet printer, and other structural members. A hydrophilic structure (100) has recesses (17) and protrusions (18) formed on the surface of the substrate. The protrusions (18) have the same height. A

hydrophilic film (20) is formed on the surfaces of the recesses (17) and the protrusions (18). The hydrophilic structure (100) is provided to the ink-ejection surface of the ink-jet printing head except the ink-ejection holes, and the ink-jet printing head is mounted on the ink-jet printer.

**FIG. 1**



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**Description**

## TECHNICAL FIELD

5 **[0001]** The present invention relates to a hydrophilic structure superior in hydrophilicity, an ink-jet recording head having an ink-jet surface superior in hydrophilicity, methods for manufacturing such a hydrophilic structure and such an ink-jet recording head, an ink-jet recording apparatus, and structural members for a micro-pump, frosted glass, a bearing, a bath tub, a bathroom tile, a wash stand, a pipe for a heat exchanger, a blood circuit for an artificial lung, etc.

## 10 BACKGROUND ART

**[0002]** In the background art, there have been devised various hydrophilic treatment methods for the purpose of preventing fogging of window glass or the like in a building, a car or the like, for the purpose of preventing fouling of a solid surface, or for other purposes. Of these hydrophilic treatment methods, JP-B-61-83106 and Japanese Patent No. 15 2756474 disclose a hydrophilic treatment method using optically semiconducting metal oxide. In this hydrophilic treatment method, optically semiconducting metal oxide such as titanium oxide or the like is formed on a solid surface, and this solid surface is irradiated with surface.

**[0003]** Incidentally, in an ink-jet recording head, glass, metal or the like is used for the constituent material of an ink-jet surface (except ink-jet holes). Therefore, when there appears a portion to which it is difficult for ink droplets to 20 adhere, for example, due to the adhesion of fat or oil from the environment, there is a fear that the linearity of ink droplets to be discharged is lost so that troubles such as printing instability or the like may hinder good recording. Thus, it is requested that either a hydrophilic state easy to get wet with ink or a water repellent state difficult to get wet with ink can be kept for a long term in the ink-jet surface of the ink-jet recording head.

**[0004]** However, the above-mentioned background-art hydrophilic treatment method using optically semiconducting metal oxide does not have such a function satisfactorily. Particularly, when the hydrophilic treatment method is 25 applied to an ink-jet recording head, it has a problem as follows.

**[0005]** That is, the hydrophilic treatment method using optically semiconducting metal oxide required irradiating the optically semiconducting metal oxide with light including an ultra-violet component, but the structure of an ink-jet recording head was so complicated that its ink-jet surface could not be always irradiated with light including an ultra-violet 30 component. As a result, any good hydrophilic state could not be obtained in a portion which was not irradiated with the light. Even if a hydrophilic state could be obtained temporarily, the hydrophilic state could not be kept over a long period of time.

**[0006]** PCT/WO96/29375 also proposes a method in which a surface of a minor lens, window glass, goggles, a bath tub, or other articles is coated with a photocatalyst semiconductor material and then irradiated with light so as to obtain 35 hydrophilicity, anti-fogging properties, and easiness in cleansing by rinsing. Even in this method, however, irradiation with light having a comparatively short wavelength is necessary so that any good hydrophilic state cannot be obtained in a portion which is not irradiated with the light. In addition, since there is a problem in durability, even if a hydrophilic state can be obtained temporarily, the hydrophilic state cannot be kept over a long period of time.

**[0007]** Further, JP-A-5-312153 proposes a method in which the surface of a channel of a micro-pump is subject to graft treatment for the purpose of preventing generation of bubbles in the channel and improving the constant flow rate 40 property. Even in this method, however, there is a possibility that any hydrophilic state cannot be kept over a long period of time because there is a problem in durability.

**[0008]** JP-A-1-250265 also proposes a method in which a blood circuit of an artificial lung is coated with HEMA or the like in order to improve its wettability with blood and its gas exchangeability. Also in this method, however, there is 45 a problem in adhesive properties of the coating polymer, and there is a disadvantage in durability.

## DISCLOSURE OF THE INVENTION

**[0009]** It is an object of the present invention to provide a hydrophilic structure which can keep hydrophilicity for a 50 long term, and a method for manufacturing such a hydrophilic structure.

**[0010]** It is another object of the present invention to provide: an ink-jet recording head in which an ink-jet surface has such a hydrophilic structure so that high printing quality can be kept for a long term; a method for manufacturing such an ink-jet recording head; and an ink-jet recording apparatus.

**[0011]** It is a further object of the present invention to provide a structural member in which a hydrophilic structure 55 is formed in the surface so as to show a hydrophilic function.

(1) According to an aspect of the present invention, there is provided a hydrophilic structure wherein desirable irregularities of protrusion portions and recess portions are formed in a surface of a base so that the surface is

hydrophilic and the protrusion portions of the surface are uniform in height.

(2) According to another aspect of the present invention, there is provided a hydrophilic structure wherein desirable irregularities of protrusion portions and recess portions are formed in a surface of a base so that the surface is hydrophilic and each of the recess portions in the surface has a depth not less than a predetermined value.

(3) According to a further aspect of the present invention, in the hydrophilic structure of the above-mentioned paragraph (1) or (2), the irregularities have such dimensions that droplets can enter the recess portions easily.

(4) According to a still further aspect of the present invention, in the hydrophilic structure of any one of the above-mentioned paragraphs (1) to (3), the protrusion portions of the irregularities are arranged in distribution, in lines, or in a lattice.

(5) According to another aspect of the present invention, in the hydrophilic structure of any one of the above-mentioned paragraphs (1) to (4), the base is silicon, silicon oxide, or glass.

(6) According to a further aspect of the present invention, in the hydrophilic structure of any one of the above-mentioned paragraphs (1) to (5), surfaces of the irregularities are subjected to hydrophilic treatment.

(7) According to a still further aspect of the present invention, in the hydrophilic structure of any one of the above-mentioned paragraphs (1) to (5), the base in which the irregularities are formed is made by using a hydrophilic base, for example glass.

(8) According to another aspect of the present invention, there is provided a method for manufacturing a hydrophilic structure of any one of the above-mentioned paragraphs (1) to (7), wherein the hydrophilic structure is manufactured by a photolithography method and an etching method. This etching method is, for example, a trench dry etching method, an anodic electrolysis method, an anisotropic wet etching method, an isotropic wet etching method, or an isotropic dry etching method.

(9) According to a further aspect of the present invention, in the method for manufacturing a hydrophilic structure of any one of the above-mentioned paragraphs (1) to (7), the irregularities of the hydrophilic structure are formed by means of a mold having a shape corresponding to the irregularities. For example, the hydrophilic structure can be obtained in such a way that a mold having a shape corresponding to the irregularities of the hydrophilic structure is pressed onto the surface of the base, or in such a way that the base which has not been hardened yet is passed along a die having a shape corresponding to the irregularities of the hydrophilic structure formed in its outer circumferential portion.

(10) According to a further aspect of the present invention, in an ink-jet recording head, an ink-jet surface except nozzle jet holes is composed of a hydrophilic structure as defined in any one of the above-mentioned paragraphs (1) to (7).

(11) According to another aspect of the present invention, there is provided a method for manufacturing an ink-jet recording head which is a method for manufacturing an ink-jet recording head of the above-mentioned paragraph (10). The hydrophilic structure is manufactured by a photolithography method and an etching method. This etching method is similar to that described in the above-mentioned paragraph (8).

(12) According to another aspect of the present invention, an ink-jet recording apparatus is mounted with an ink-jet recording head according to the above-mentioned paragraph (10).

(13) According to another aspect of the present invention, a structural member is composed of a hydrophilic structure according to the above-mentioned paragraphs (1) to (7). For example, the structural member is applied to a micro-pump, a blood circuit for an artificial lung, frosted glass, a bearing, a bath tub, a bath-tub tile, a wash stand, a path (pipe) for a heat exchanger, etc.

**[0012]** The hydrophilic structure according to the present invention has a structure in which an artificial irregular shape is provided on a base to thereby obtain not only a stable super hydrophilic function but also high durability and high mar-proof property. In addition, the ink-jet surface except the ink discharge holes in the ink-jet recording head is designed to have a hydrophilic structure so that the hydrophilic performance with respect to ink is improved. As a result,

the printing quality becomes superior for a long term. Further, since the hydrophilic structure according to the present invention is manufactured by a photolithography method and an etching method, it is possible to make the protrusion portions uniform in height with precision, and it is also possible to manufacture a reproducible hydrophilic structure. In addition, also in a structural member to which the above-mentioned hydrophilic structure is applied, a stable super hydrophilic function, high durability and high mar-proof property are obtained.

**[0013]** According to the present invention, not only a super hydrophilic function but also high durability and high mar-proof property are obtained by the above-mentioned hydrophilic structure. The details of the present invention including its operation principle will be explained in Embodiment 1 which will be described below. Further, according to the present invention, it is defined that the conception of super hydrophilic includes super lipophilic.

## BRIEF DESCRIPTION OF THE DRAWINGS

### **[0014]**

Fig. 1 is an explanatory view of a structure according to Embodiment 1 of the present invention;

Fig. 2 is a view for explaining the dimensions of a recess portion and a protrusion portion in Fig. 1;

Fig. 3 shows different plan views of the structure 100 in Fig. 1;

Fig. 4 is an exploded perspective view of an ink-jet recording head according to Embodiment 2 of the present invention;

Fig. 5 is a series of sectional views showing a manufacturing process for forming a structure on the surface of a second plate in Embodiment 2;

Fig. 6 is a top view of the second plate on which the structure is formed;

Fig. 7 is a series of sectional views showing a manufacturing process for a second plate in a Comparative Example;

Fig. 8 is a series of sectional views showing a manufacturing process for forming a structure on the surface of a second plate in Embodiment 3 of the present invention;

Fig. 9 is a series of sectional views showing a manufacturing process for forming a structure on the surface of a second plate in Embodiment 4 of the present invention;

Fig. 10 is a series of sectional views showing a manufacturing process for forming a structure on the surface of a second plate in Embodiment 5 of the present invention;

Fig. 11 is a series of sectional views showing a manufacturing process for forming a structure on the surface of a second plate in Embodiment 6 of the present invention;

Fig. 12 is an explanatory view showing an example of a mechanism near an ink-jet head manufactured through any one of the manufacturing processes of Embodiments 2 to 6;

Fig. 13 is an external appearance view of an ink-jet recording apparatus on which the mechanism of Fig. 12 is mounted;

Fig. 14 is a sectional view of a micro-pump according to Embodiment 9 of the present invention;

Fig. 15 depicts explanatory views showing a mechanism for manufacturing a tube in Fig. 14;

Fig. 16 shows sectional views of different frosted glass according to Embodiment 10 of the present invention;

Fig. 17 is a sectional view of a mechanism for a watch according to Embodiment 11 of the present invention; and

Fig. 18 shows perspective views of a bathroom and a wash stand according to Embodiment 12 of the present invention.

## THE BEST MODE FOR CARRYING OUT THE INVENTION

Embodiment 1.

5 **[0015]** Fig. 1 is an explanatory view of a hydrophilic structure according to Embodiment 1 of the present invention. In Fig. 1, in a hydrophilic structure 100, recess portions 17 and protrusion portions 18 are formed on the surface of a silicon substrate 11, and a hydrophilic film 20 is formed on the surfaces of the recess portions 17 and the protrusion portions 18. In this structure, in addition to the performance of the hydrophilic film 20, fluid 21 permeates into the recess portions 17 by capillarity so that the hydrophilicity of the surface of the structure is improved. Therefore, these irregularities are adjusted to dimensions such that the fluid 21 can enter the recess portions 17 easily by capillarity. After formation of the irregularities, the hydrophilic film 20 may be formed, for example, by graft polymerizing, silica coupling, silicon oxidizing, or the like. In this embodiment, since the silicon substrate 11 is used as the base, the hydrophilic film 20 is formed by silicon oxidizing. Although this embodiment shows the case where the hydrophilic film 20 is formed, a base having a hydrophilic function, for example, glass, or the like, may be used with irregularities formed thereon.

15 **[0016]** Fig. 2 is a view for explaining the dimensions of each recess portion 17 and each protrusion portion 18 in Fig. 1. In Fig. 2, the symbol A designates a protrusion width (depending on the mask design); B, a groove width (depending on the mask design); C, a working quantity (depending on the depth and etching time); and D, a side wall angle (depending on the etching conditions).

**[0017]** In the case of an ink-jet recording apparatus for jetting ink droplets each having a diameter of tens of  $\mu\text{m}$ , the above-mentioned widths A and B are restricted by themselves in order to obtain stable hydrophilic performance near nozzle holes. In addition, the above-mentioned quantity C needs to have a certain degree of depth enough to diffuse permeating ink droplets in the recess portion stably. Therefore, the above-mentioned widths A and B are restricted in a range of from 0.2 to 500  $\mu\text{m}$ , preferably from 0.5 to 30  $\mu\text{m}$ , more preferably from 1 to 10  $\mu\text{m}$ . In addition, the above-mentioned quantity C is restricted to a depth of 1  $\mu\text{m}$  or more, preferably 3  $\mu\text{m}$  or more, more preferably 5  $\mu\text{m}$  or more. The evenness of the height of the protrusion portions is restricted within 0.5 times as large as the value of the widths A and B, preferably within 0.3 times, more preferably within 0.1 times, from the point of view of the mar-proof property.

**[0018]** Fig. 3 is a plan view of the hydrophilic structure 100 in Fig. 1. Fig. 3(A) shows an example in which the protrusion portions 18 are distributed regularly. Fig. 3(B) shows an example in which the protrusion portions 18 are arranged in the form of lines. Fig. 3(C) shows an example in which the protrusion portions 18 are arranged in the form of a lattice. Although Fig. 3(A) shows an example in which the protrusion portions 18 are square prisms, they may be various pillars such as triangular prisms, pentagonal prisms, hexagonal prisms, circular columns, etc., or cones.

Embodiment 2.

35 **[0019]** Fig. 4 is an exploded perspective view of an ink-jet recording head according to Embodiment 2 of the present invention. As illustrated, the ink-jet recording head has a configuration in which a first plate 1 and a second plate 2 are laminated on each other so that an ink supply portion 3, pressure chambers 4 for jetting ink, and channels 5 for passing the ink therethrough are formed. The pressure chambers 4 jet ink by using vibration of a diaphragm such as an electrostatic diaphragm vibrated by static electricity, a piezoelectric vibrator such as an PZT, or the like, or by heating of a heating element. In the second plate 2, nozzle holes 6 are formed perpendicularly to the channels 5. The hydrophilic structure 100 in Fig. 1 is formed on the surface of the second plate 2, and the hydrophilic film 20 is formed on the surface of the hydrophilic structure 100.

**[0020]** Fig. 5 is a sectional view showing a manufacturing process for forming the hydrophilic structure on the surface of the second plate 2. Fig. 6 is a top view of the second plate 2 in which the hydrophilic structure has been formed on the surface. Here, description will be made about the case where the surface of a silicon substrate is worked by a photolithography method and a trench dry etching method so that a hydrophilic structure is formed.

① First, a 4-inch single-crystal silicon wafer of the (100) crystal orientation is prepared as the base of the second plate 2. As shown in Fig. 5(a), a silicon oxide film 12 having a thickness of about 1,000 Angstroms is formed on at least one surface of the single-crystal silicon substrate 11 by use of a thermal oxidation method.

② Next, as shown in Fig. 5(b), about 2 ml of photosensitive resin OFPR-800 (viscosity; 30 cps) made by TOKYO OHKA KOGYO CO., LTD. is dropped onto the thermally oxidized silicon film 12 of the single-crystal silicon substrate 11, and spin-coated for 30 seconds at the velocity of 5,000 rotations per minute, so that a photosensitive resin layer 13 is formed. By these spin-coat conditions, the photosensitive resin can be applied so that the average film thickness is about 1  $\mu\text{m}$ , and the variation in the wafer surface is 10%. Then, the coating film thickness is changed desirably in accordance with the dimensions of a groove to be worked, or the like. The maximum value of the thickness of the photosensitive material film to be applied is 2  $\mu\text{m}$  when the dimension of one side of the groove is 2  $\mu\text{m}$ .

③ Next, the substrate 11 is dried for 30 minutes in an oven at a temperature of 90°C, and cooled down to the room temperature. As shown in Fig. 5(c), protrusion-portion-expected areas 13 each of which is 0.2μm to 200μm square are photolitho-patterned in the substrate 11. Then, the photosensitive resin is solidified by the oven at a temperature of 120°C, so that the etching-proof property is improved.

④ As shown in Fig. 5(d), the silicon oxide film in groove-expected areas is etched with fluoric acid, and the photo-sensitive resin is removed in a stripping solution.

⑤ Next, by use of a trench dry etching apparatus, a plasma synthetic film 14 is formed with gas containing C and F, as shown in Fig. 5(e). Succeedingly, after the dry etching apparatus has been evacuated, silicon in the area of a silicon substrate bottom 15 is etched with plasma of gas of the chemical formula SF<sub>6</sub> or CF<sub>4</sub>, as shown in Fig. 5(f). Then, as shown in Fig. 5(f), the silicon oxide film 12 exists in portions which shall be protrusion portions, so that the portions are not etched. On the other hand, portions which shall be recess portions are anisotropically etched effectively by the effect of the plasma synthetic film formed on portions which shall be side walls of the protrusion portions. Such a plasma synthesis step and such a plasma etching step are repeated. As a result, grooves each having a depth of about 5μm are etched in the surface of the single-crystal silicon substrate 11 so that the recess portions 17 and the protrusion portions 18 are formed, as shown in Fig. 5(g). These protrusion portions 18 are laid out regularly on the surface of the single-crystal silicon substrate 11, as shown in Fig. 3.

⑥ Next, nozzle holes 6 (see Fig. 4) are worked, and a silicon oxide film is formed on the single-crystal silicon substrate 11 by a thermal oxidation method (alternatively, a sputtering method or a sol-gel method may be used) so as to obtain a hydrophilic film 20 (Fig. 5(h)).

⑦ Finally, a first plate 1 is bonded with the second plate 2 formed thus so that an ink-jet recording head is completed.

(Example 1)

**[0021]** As Example 1 of the present invention, examples shown in Table 1 were attempted in the above-mentioned Embodiment 2. First, base materials of samples 1 to 7 were prepared for the substrate 11 of the second plate. Then, the protrusion-portion-expected areas 13 (see Fig. 5(c)) were formed by patterning squares each in a range of from 0.2 μm to 1,000 μm. In addition, the hydrophilic film to be formed on the second plate 2 was formed by depositing silicon oxide.

**[0022]** This hydrophilic treatment was not performed on the samples 2, 4 and 6.

[Table 1]

Number	Base	Protrusion size (micron square)	Hydrophilic treatment
Sample 1	Single-crystal silicon	0.2	Yes
Sample 2	Single-crystal silicon	0.2	No
Sample 3	Glass	5	Yes
Sample 4	Single-crystal silicon	5	No
Sample 5	Quartz	10	Yes
Sample 6	Single-crystal silicon	10	No
Sample 7	Quartz	500	Yes
Sample 8	Glass	500	No

(Comparative Example)

**[0023]** Fig. 7 is a sectional view showing a manufacturing process as a Comparative Example in which hydrophilic treatment is applied to a second plate of stainless steel in an ink-jet recording head configured in the same manner as in Embodiment 2. The ink-jet recording head in this Comparative Example has the same configuration as that shown in

Fig. 4.

① First, a base 31 for the second plate was worked so that nozzle holes 32 were formed. Then, the base 31 was subjected to ultrasonic cleaning with an alkali detergent, as shown in Fig. 7(a).

② Next, as shown in Fig. 7(b), titanium oxide 33 was deposited on the second plate base 31.

③ Finally, a first plate 1 was bonded with the second plate 2 formed thus so that an ink-jet recording head was completed.

**[0024]** Table 2 shows contact angles of the second plates against ink and water in this Example and Comparative Example. Further, data of Comparative Example were obtained immediately after irradiation with ultra-violet rays.

[Table 2]

Number		Water contact angle (degrees)	Ink contact angle (degrees)
Example	Sample 1	6	2
	Sample 2	20	12
	Sample 3	4	2
	Sample 4	30	14
	Sample 5	4	4
	Sample 6	30	16
	Sample 7	20	10
	Sample 8	20	10
Comparative Example		10	4

**[0025]** Each sample, except those which used silicon not-subjected to hydrophilic treatment, was superior in hydrophilicity with the contact angle against ink not more than 10 degrees.

**[0026]** Each ink-jet recording head in Embodiment 1 was mounted on a recording apparatus, and subjected to a printing test in initial conditions and in accelerated conditions corresponding to 2 years in the darkness. Thus, the results were obtained as shown in Table 3. Table 3 shows the results of judgement upon printing quality, in which the mark © designates superior printing quality without ink mist adhering to the second plate surface; the mark ○, superior printing quality though ink mist adhered to the second plate surface; and the mark X, defective due to bending in flying of ink.

[Table 3]

Sample number		Printing quality	
		Initial	After accelerated conditions corresponding to 2 years
Example	Sample 1	⊙	⊙
	Sample 2	○	○
	Sample 3	⊙	⊙
	Sample 4	○	○
	Sample 5	⊙	⊙
	Sample 6	○	○
	Sample 7	⊙	○
	Sample 8	○	○
Comparative Example		⊙	X

**[0027]** As described above, in the ink-jet recording heads in Example 1, printing quality was superior and reproducibility was also confirmed in the initial conditions and in the accelerated conditions corresponding to 2 years. Of them, the printing quality of the second plate which has protrusion portions in a range of from 0.2  $\mu\text{m}$  to 500  $\mu\text{m}$  and which is coated with a hydrophilic agent to thereby form a hydrophilic film aggressively was superior. However, in the Comparative Example, the hydrophilic performance was lowered and the printing quality also deteriorated due to the environment where light could not reach.

(Example 2)

**[0028]** In Example 2 of the present invention, examination was made about the contact angles between water/ink and the protrusion shapes of hydrophilic structures which were arranged in tetragonal prisms, in lines and in the form of a lattice (see Figs. 3(A), (B) and (C)). Table 4 shows data of those angles. It is understood that each of the hydrophilic structures according to the present invention had a contact angle of ink of 10 degrees or less so as to obtain superior hydrophilic performance without irradiation with ultra-violet rays.

[Table 4]

No.	Structure dimensions					Contact angle	
	Structure	Protrusion width A( $\mu\text{m}$ )	Groove width B( $\mu\text{m}$ )	Working quantity C( $\mu\text{m}$ )	Side wall angle D( $^\circ$ )	Pure water ( $^\circ$ )	Ink ( $^\circ$ )
1	Square columns	0.2	2.4	3.2	14	6	2
2	Square columns	1.0	6.0	6.8	1	10	4
3	Square columns	4.0	6.0	8.6	0	12	6
4	Lines	1.2	2.0	7.8	1	10	4
5	Lines	4.0	6.0	8.0	4	12	4
6	Lattice	4.3	6.0	10.0	2	10	8
7	Lattice	10.0	6.0	1.2	14	8	6



(Example 3)

**[0029]** By use of resin as the raw material, molding was performed with the structure of Example 1 or 2 as a mold. The surface of a molded product obtained thus had a pattern of irregularities which was transferred from the surface of the mold. It was confirmed that such a structure subjected to hydrophilic treatment also had superior properties similar to those in Examples 1 and 2.

#### Embodiment 3.

**[0030]** Fig. 8 is a sectional view showing a process for manufacturing an ink-jet recording head according to Embodiment 3 of the present invention. Fig. 8 shows a manufacturing process for forming a hydrophilic structure on the surface of a second plate 2. Here, description will be made about the case where the surface of a silicon substrate is worked by a photolithography method and an anodic electrolysis method so that a hydrophilic structure is formed.

① First, for example, a 200 $\mu$ m thick n-type single-crystal silicon substrate 11 of (100) plane orientation is prepared as the base of a second plate.

② Silicon nitride films 23 and 24 of 0.3 $\mu$ m thick are formed as etching-proof coatings on this silicon substrate 11 by a CVD apparatus, as shown in Fig. 8(a).

③ Next, after the silicon nitride film 24 is removed by a dry etching method, photolitho-etching is given to the silicon nitride film 23 so that the silicon nitride film 23 is etched in portions 22 corresponding to the recess portions 17 of the structure, as shown in Fig. 8(b).

④ Next, etching pyramids 25 shaped into V-grooves are worked in the silicon substrate 11 by an anisotropic etching method using an aqueous solution of potassium hydrate with the silicon nitride film 23 as a mask. An indium-tin oxide film (ITO film) 26 is formed on the surface of the silicon substrate 11 opposite to the surface where the silicon nitride film 23 has been formed, as shown in Fig. 8(c).

⑤ Succeedingly, an electrolytic cell is assembled so that the above-mentioned surface where the silicon nitride film 23 has been formed is in contact with electrolyte. While the silicon substrate 11 is irradiated with light at its surface opposite to the surface where the silicon nitride film 23 has been formed, grooves 27 of about 5 $\mu$ m deep are etched as shown in Fig. 8(d), so that the recess portions 17 and the protrusion portions 18 are produced (Fig. 8(e)).

⑥ Nozzle holes 6 (see Fig. 4) are worked, and a silicon oxide film is deposited as the hydrophilic film 20 on the second plate 2 by a vacuum deposition method (Fig. 8(f)).

⑦ Finally, a first plate 1 is bonded with the second plate 2 formed thus so that an ink-jet recording head is completed.

#### Embodiment 4.

**[0031]** Fig. 9 is a sectional view showing a process for manufacturing an ink-jet recording head according to Embodiment 4 of the present invention. Fig. 9 shows a manufacturing process for forming a hydrophilic structure on the surface of a second plate 2. Here, description will be made about the case where the surface of a silicon substrate is worked by a photolithography method and an anisotropic wet etching method so that a hydrophilic structure is formed.

① First, a 4-inch single-crystal silicon wafer of the (100) crystal orientation is prepared as the base of the second plate 2. A silicon oxide film 112 having a thickness of about 1,000 Angstroms is formed on at least one surface of a single-crystal silicon substrate 111 by use of a thermal oxidation method, as shown in Fig. 9(a).

② Next, as shown in Fig. 9(b), about 2 ml of photosensitive resin OFPR-800 (viscosity: 30 cps) made by TOKYO OHKA KOGYO CO., LTD. is dropped onto the thermally oxidized silicon film 112 of the single-crystal silicon substrate 111, and spin-coated for 30 seconds at the velocity of 5,000 revolutions per minute, so that a photosensitive resin layer 113 is formed. By these spin-coat conditions, the photosensitive resin can be applied so that the average film thickness is about 1 $\mu$ m, and the variation in the wafer surface is 10%. Then, the coating thickness is changed desirably in accordance with the dimensions of a groove to be worked, or the like. The maximum value of the thickness of the photosensitive material film to be applied is 2 $\mu$ m when the dimension of one side of the groove is 2 $\mu$ m.

③ Next, the substrate 111 is dried for 30 minutes in an oven at a temperature of 90°C, and cooled down to the room temperature. As shown in Fig. 9(c), protrusion-portion-expected areas 113, each 0.2μm to 200μm square, are photolitho-patterned so as to be left on the substrate 111. Then, the photosensitive resin is solidified by the oven at a temperature of 120°C, so that the etching-proof property is improved.

④ As shown in Fig. 9(d), the silicon oxide film in groove-expected areas is etched with fluoric acid, and the photo-sensitive resin is removed in a stripping

⑤ Next, sectionally V-shaped etching pyramids 114 are formed in the silicon substrate 111 by an anisotropic etching method using an aqueous solution of potassium hydrate with the silicon oxide film 112 as a mask, as shown in Fig. 9(e). Then, the silicon oxide film 112 is removed (Fig. 9(f)). The etching pyramids 114 formed thus correspond to the recess portions 17 in Fig. 1. Producing the recess portions 17 results in producing the protrusion portions 18 inevitably, so that the protrusion portions 18 are laid out regularly on the surface of the single crystal silicon substrate 111, as shown in Fig. 6.

⑥ Next, nozzle holes 6 (see Fig. 4) are worked, and a silicon oxide film is deposited as the hydrophilic film 20 on the single-crystal silicon substrate 111 by a vacuum deposition method (Fig. 9(g)).

⑦ Last, a first plate 1 is bonded with the second plate 2 formed thus so that an ink-jet recording head is completed.

#### Embodiment 5.

**[0032]** Fig. 10 is a sectional view showing a process for manufacturing an ink-jet recording head according to Embodiment 5 of the present invention. Fig. 10 shows a manufacturing process for forming a porous structure on the surface of a second plate 2. Here, description will be made about the case where the surface of a silicon substrate is worked by a photolithography method and an isotropic wet etching method so that a porous structure is formed.

① First, for example, a 200μm thick glass substrate 211 is prepared as the base of the second plate 2.

② Next, as shown in Fig. 10(b), a silicon nitride film 212 of 0.3 μm thick is formed as an etching-proof coating on this glass substrate 211 by a sputtering apparatus.

③ Next, photolitho-etching is given to the silicon nitride film 212 so that the silicon nitride film is etched in portions corresponding to the recess portions 17 of the structure, as shown in Fig. 10(b).

④ Next, as shown in Fig. 10(c), etching recess portions 215 are worked in the glass substrate 211 by an isotropic etching method using an aqueous solution of hydrofluoric acid with the silicon nitride film 212 as a mask.

⑤ Next, as shown in Fig. 10(d), the silicon nitride film 212 is removed with hot phosphoric acid so that the irregularities are completed.

⑥ Next, nozzle holes 6 (see Fig. 4) are worked, and a silicon oxide film is deposited as the hydrophilic film 20 on the glass substrate 211 by a vacuum deposition method (Fig. 10(e)).

⑦ Finally, a first plate 1 is bonded with the second plate 2 formed thus so that an ink-jet recording head is completed.

#### Embodiment 6.

**[0033]** Fig. 11 is a sectional view showing a process for manufacturing an ink-jet recording head according to Embodiment 6 of the present invention. Fig. 11 shows a manufacturing process for forming a porous structure on the surface of a second plate 2. Here, description will be made about the case where the surface of a silicon substrate is worked by a photolithography method and an isotropic dry etching method so that a porous structure is formed.

① First, for example, a 200μm thick glass substrate 311 is prepared as the base of the second plate 2.

② Next, a photosensitive resin film 312 of about 5μm thick is formed as the etching-proof coating on this glass substrate 311 by a spin-coat apparatus, as shown in Fig. 11(a).

③ Next, the photosensitive resin film 312 is etched in portions corresponding to the recess portions 17 in the structure by photolitho-etching, as shown in Fig. 11(b).

④ Next, etching recess portions 315 are worked in the glass substrate 311 by an isotropic plasma etching method using CF<sub>4</sub> gas with the photosensitive resin film as a mask, as shown in Fig. 11(c).

⑤ Next, the photosensitive resin film 312 is removed with hot sulfuric acid so that the irregularities are completed, as shown in Fig. 11(d).

⑥ Next, nozzle holes 6 (see Fig. 4) are worked, and a silicon oxide film is deposited as the hydrophilic film 20 on the glass substrate 311 by a vacuum deposition method (Fig. 11(e)).

⑦ Finally, a first plate 1 is bonded with the second plate 2 formed thus so that an ink-jet recording head is completed.

**[0034]** Also in the hydrophilic structures produced in the above-mentioned Embodiments 4 to 6, it has been confirmed that the protrusion portions are even in height, and it is therefore possible to obtain a hydrophilic function, durability and mar-proof property similar to those in the above-mentioned Embodiment 2.

**[0035]** In the above-mentioned Embodiments 2 to 6, a hydrophilic structure is produced by a photolithography method and an etching method, and the surface of the base of the hydrophilic structure can be replaced by the tops of protrusion portions. Accordingly, the protrusion portions inevitably become even in height with high precision.

**[0036]** In addition, although examples using silicon or glass substrates as the material of the second plate 2 were described in the above-mentioned Embodiments 2 to 6, the material of the second plate 2 is not limited to those materials in the present invention. Similar functions can be shown even in metal material such as stainless steel or organic polymeric material.

#### Embodiment 7.

**[0037]** Fig. 12 is an explanatory view showing an example of a mechanism near an ink-jet head manufactured through any one of the manufacturing processes of Embodiments 2 to 6. An ink-jet head 50 is attached to a carriage 51, and this carriage 51 is movably attached to guide rails 52. Then, the position of the carriage 51 is controlled in the width direction of paper 54 fed by a roller 53. This mechanism in Fig. 12 is mounted on an ink-jet recording apparatus 55 shown in Fig. 13. It has been confirmed that high-quality printing can be obtained in printing with this ink-jet recording apparatus 55. Particularly, with respect to rubbing in cleaning, it has been confirmed that a hydrophilic function is obtained by the structure of the base material of the ink-jet head so that the ink-jet head has abrasion resistance enough to be proof against long-term use.

#### Embodiment 8.

**[0038]** Fig. 14 is a sectional view of a micro-pump according to Embodiment 8 of the present invention. In Fig. 14, when a piezoelectric element 69 is driven to vibrate a diaphragm 70, fluid sucked from an inlet 65 is discharged from an outlet 66 through a closed space 71. The hydrophilic structure according to the above-mentioned Embodiments is formed on the surface of a channel including the closed space 71. A micro-pump having an extremely constant flow rate without producing any bubble in the channel when the micro-pump was actually driven to flow pure water into the channel could be realized because the above-mentioned hydrophilic structure was formed in the micro-pump as mentioned above.

**[0039]** Figs. 15(A) and (B) are explanatory views showing a mechanism for manufacturing a tube 73 communicating with the inlet 65 or the outlet 66 in Fig. 14. Fig. 15(A) is a front sectional view, and Fig. 15(B) is an enlarged sectional view taken on line B-B in Fig. 15(A). In this mechanism, for example, polyvinyl chloride accommodated in a vessel 75 is discharged in the state where a die 76 on which protrusion and recess portions have been formed is passed through a discharge portion of the vessel 75, so that irregularities are formed on the inner wall of each tube 73.

#### Embodiment 9.

**[0040]** Figs. 16(A) and (B) are sectional views of frosted glass according to Embodiment 9 of the present invention. As shown in Figs. 16(A) and (B), a hydrophilic structure 82 is formed on the surface of each frosted glass 80, 81. Accordingly, it is difficult for dirt to adhere to the surface, and even if dirt adheres to the surface, it is possible to remove the dirt easily.

Embodiment 10.

**[0041]** Fig. 17 is a sectional view showing a mechanism for a watch according to Embodiment 10 of the present invention. As shown in Fig. 17, a hydrophilic structure is formed on the inner wall of each of bearing portions 85 to 90. In this case, however, this hydrophilic structure is requested to have lipophilicity as well as hydrophilicity. It is therefore necessary to perform such a hydrophilic treatment that hydrophilic and lipophilic properties can be obtained after the treatment (hydrophilic/lipophilic treatment). Since the surface of a structure subjected to such a hydrophilic/lipophilic treatment is superior in hydrophilicity and lipophilicity, lubricating oil is retained for a long term. For example, even if the watch is driven without oiling equivalently to 10 years, the watch works normally.

Embodiment 11.

**[0042]** Figs. 18(A) and (B) are perspective views of a bathroom and a wash stand according to Embodiment 11 of the present invention. Hydrophilic structures 100 according to the above-mentioned Embodiments are formed on the surfaces of a bath tub 91, bathroom files 92 and a wash stand 93. It is therefore difficult for dirt to adhere to the surfaces, and even if dirt adheres thereto, it is possible to remove the dirt easily.

Embodiment 12.

**[0043]** The hydrophilic structure according to the present invention is usable in various applications. For example, the hydrophilic structure may be formed on the inner wall of a pipe of a heat exchanger so as to improve its thermal efficiency. Also, the hydrophilic structure may be formed on the inner wall of a blood circuit of an artificial lung so as to improve its gas exchangeability or the like.

**Claims**

1. A hydrophilic structure characterized in that desirable irregularities of protrusion portions and recess portions are formed on a surface of a base, said surface is hydrophilic, and said protrusion portions of said surface are uniform in height.
2. A hydrophilic structure characterized in that desirable irregularities of protrusion portions and recess portions are formed on a surface of a base, said surface is hydrophilic, and each of said recess portions of said surface has a depth not less than a predetermined value.
3. A hydrophilic structure according to Claim 1 or 2, characterized in that said irregularities have such dimensions that droplets can enter said recess portions easily.
4. A hydrophilic structure according to any one of Claims 1 to 3, characterized in that in said irregularities, said protrusion portions are arranged in distribution, in lines, or in a lattice.
5. A hydrophilic structure according to any one of Claims 1 to 4, characterized in that said base is silicon, silicon oxide, or glass.
6. A hydrophilic structure according to any one of Claims 1 to 5, characterized in that surfaces of said irregularities are subjected to hydrophilic treatment.
7. A hydrophilic structure according to any one of Claims 1 to 5, characterized in that said base in which said irregularities are formed is a hydrophilic base.
8. A method for manufacturing a hydrophilic structure as defined in any one of Claims 1 to 7, characterized in that said hydrophilic structure is manufactured by a photolithography method and an etching method.
9. A method for manufacturing a hydrophilic structure as defined in Claim 8, characterized in that said etching method is a trench dry etching method.
10. A method for manufacturing a hydrophilic structure as defined in Claim 8, characterized in that said etching method is an anodic electrolysis method.

11. A method for manufacturing a hydrophilic structure as defined in Claim 8, characterized in that said etching method is an anisotropic wet etching method.
- 5 12. A method for manufacturing a hydrophilic structure as defined in Claim 8, characterized in that said etching method is an isotropic wet etching method.
13. A method for manufacturing a hydrophilic structure as defined in Claim 8, characterized in that said etching method is an isotropic dry etching method.
- 10 14. A method for manufacturing a hydrophilic structure as defined in any one of Claims 1 to 7, characterized in that said irregularities of said hydrophilic structure are formed by means of a mold having a shape corresponding to said irregularities.
- 15 15. A method for manufacturing a hydrophilic structure according to Claim 14, characterized in that a mold having a shape corresponding to said irregularities of said hydrophilic structure is pressed onto the surface of said base.
- 20 16. A method for manufacturing a hydrophilic structure according to Claim 14, characterized in that before said base is hardened, said base is passed along a die having a shape which is formed in an outer circumferential portion of said die correspondingly to said irregularities of said hydrophilic structure.
- 25 17. An ink-jet recording head characterized in that an ink-jet surface except nozzle jet holes is composed of a hydrophilic structure as defined in any one of Claims 1 to 7.
18. A method for manufacturing an ink-jet recording head as defined in Claim 17, characterized in that said hydrophilic structure is manufactured by a photolithography method and an etching method.
- 30 19. A method for manufacturing an ink-jet recording head according to Claim 18, characterized in that said etching method is a trench dry etching method.
- 35 20. A method for manufacturing an ink-jet recording head according to Claim 18, characterized in that said etching method is an anodic electrolysis method.
21. A method for manufacturing an ink-jet recording head according to Claim 18, characterized in that said etching method is an anisotropic wet etching method.
- 40 22. A method for manufacturing an ink-jet recording head according to Claim 18, characterized in that said etching method is an isotropic wet etching method.
23. A method for manufacturing an ink-jet recording head according to Claim 18, characterized in that said etching method is an isotropic dry etching method.
- 45 24. An ink-jet recording apparatus characterized in that an ink-jet recording head as defined in Claim 17 is mounted on said apparatus.
- 50 25. A structural member wherein a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in a surface of said structural member.
26. A micro-pump characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in an inner wall surface of said micro-pump.
- 55 27. Frosted glass characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in a surface of said frosted glass.
28. A bearing characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is provided in a portion which is in contact with a support shaft.
29. A bath tub characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in a surface of said bath tub.

**30.** A bathroom tile characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in a surface of said bathroom tile.

5 **31.** A wash stand characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in a surface of said wash stand.

**32.** A pipe for a heat exchanger characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in an inner circumferential surface of said pipe.

10 **33.** A blood circuit for an artificial lung characterized in that a hydrophilic structure as defined in any one of Claims 1 to 7 is formed in an inner wall surface of said blood circuit.

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FIG. 1

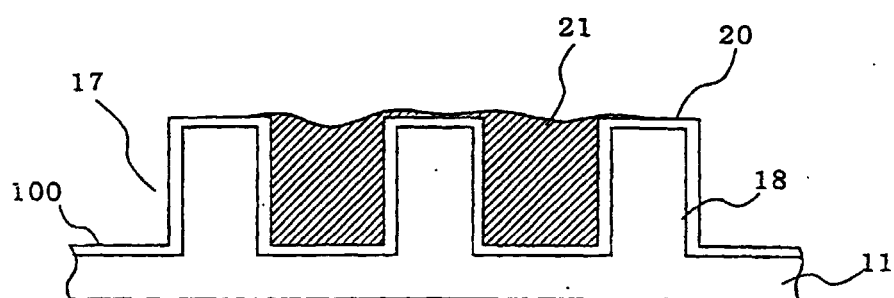


FIG. 2

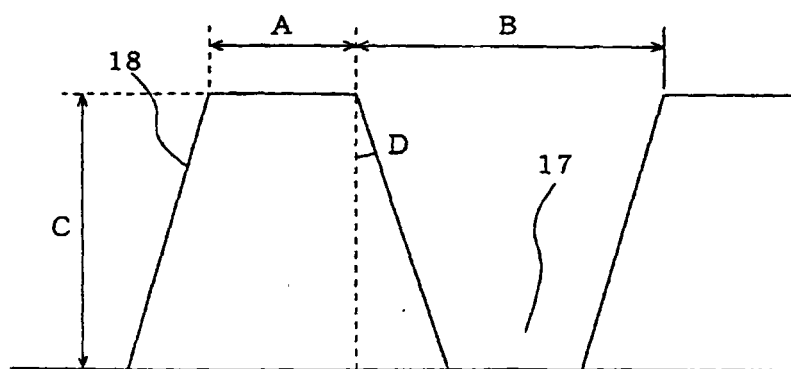


FIG. 3

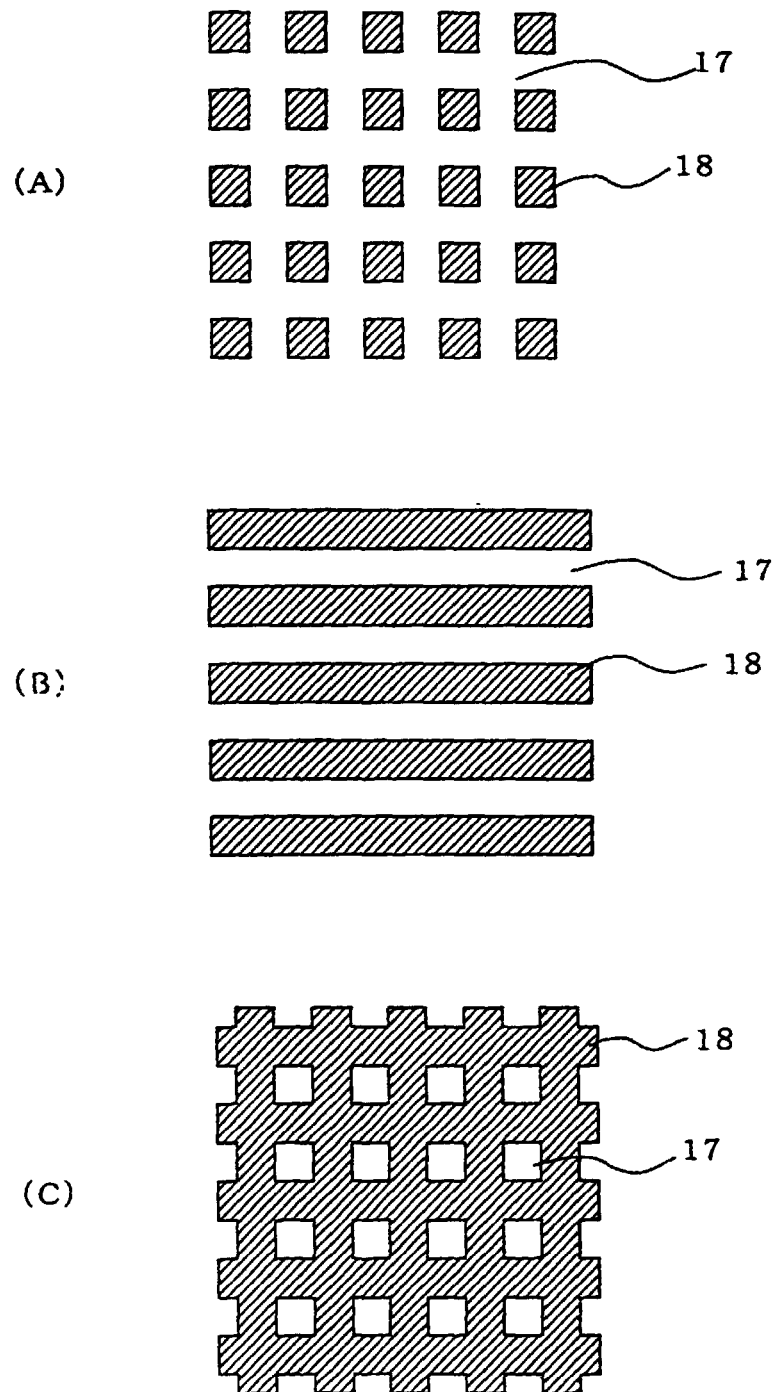




FIG. 4

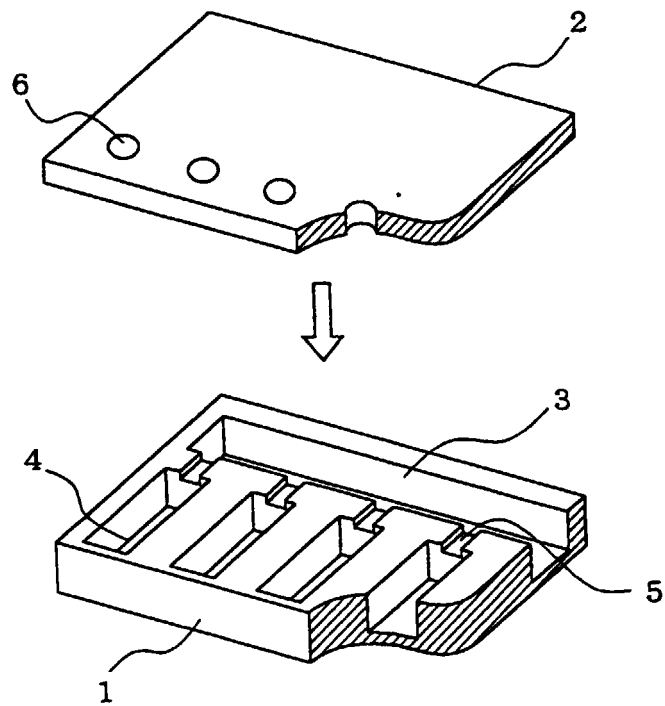


FIG. 5

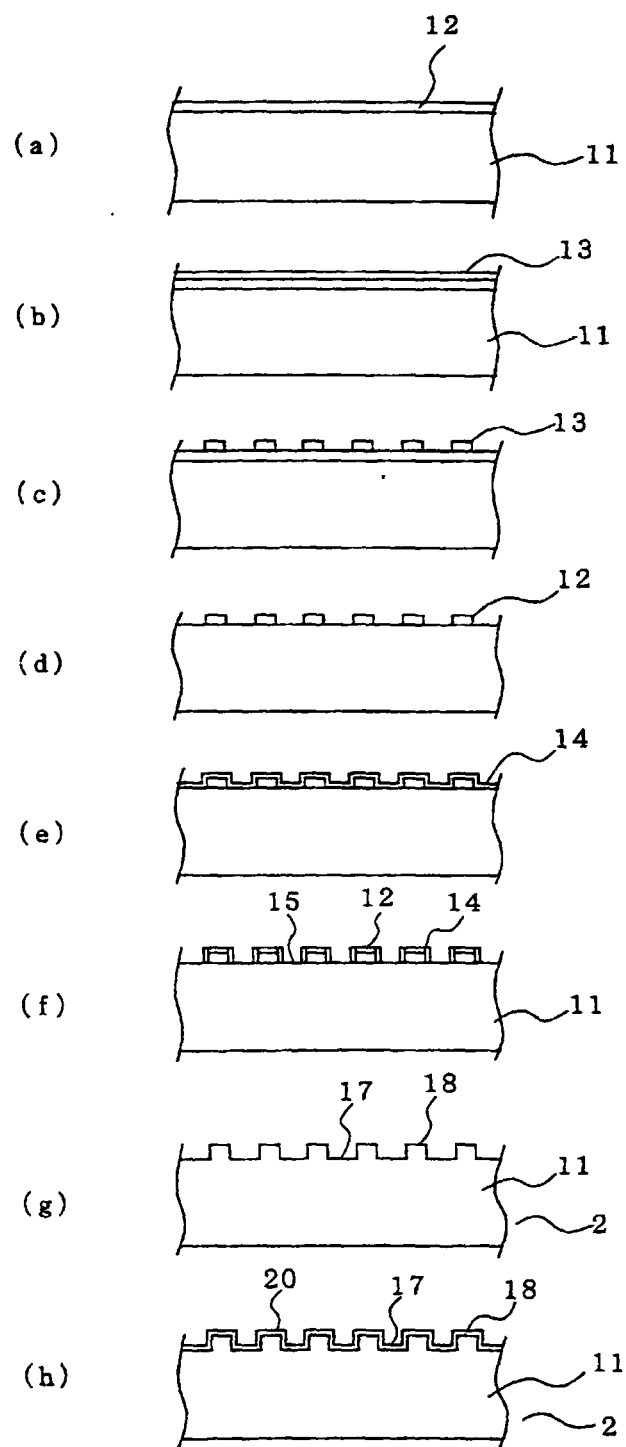


FIG. 6

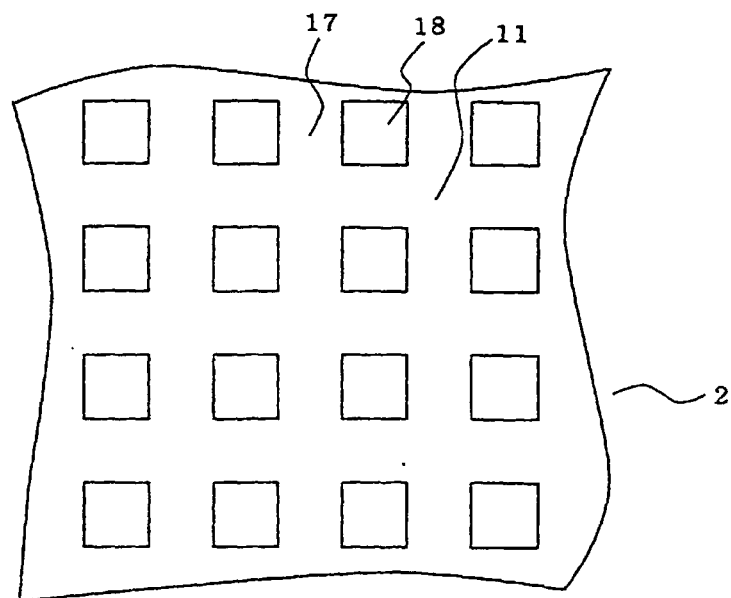


FIG. 7

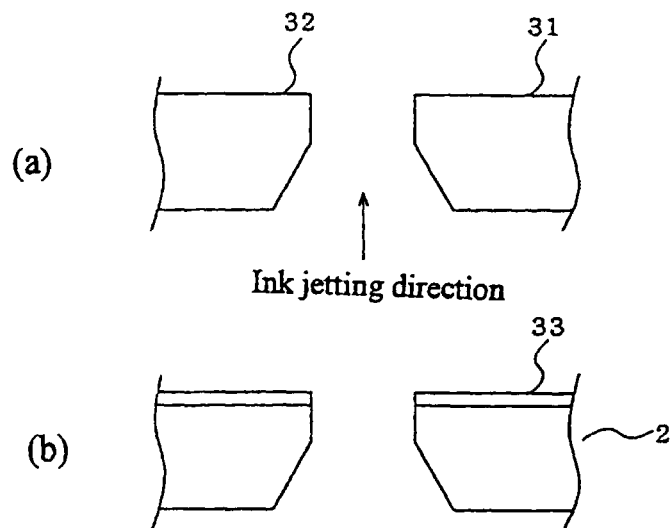


FIG. 8

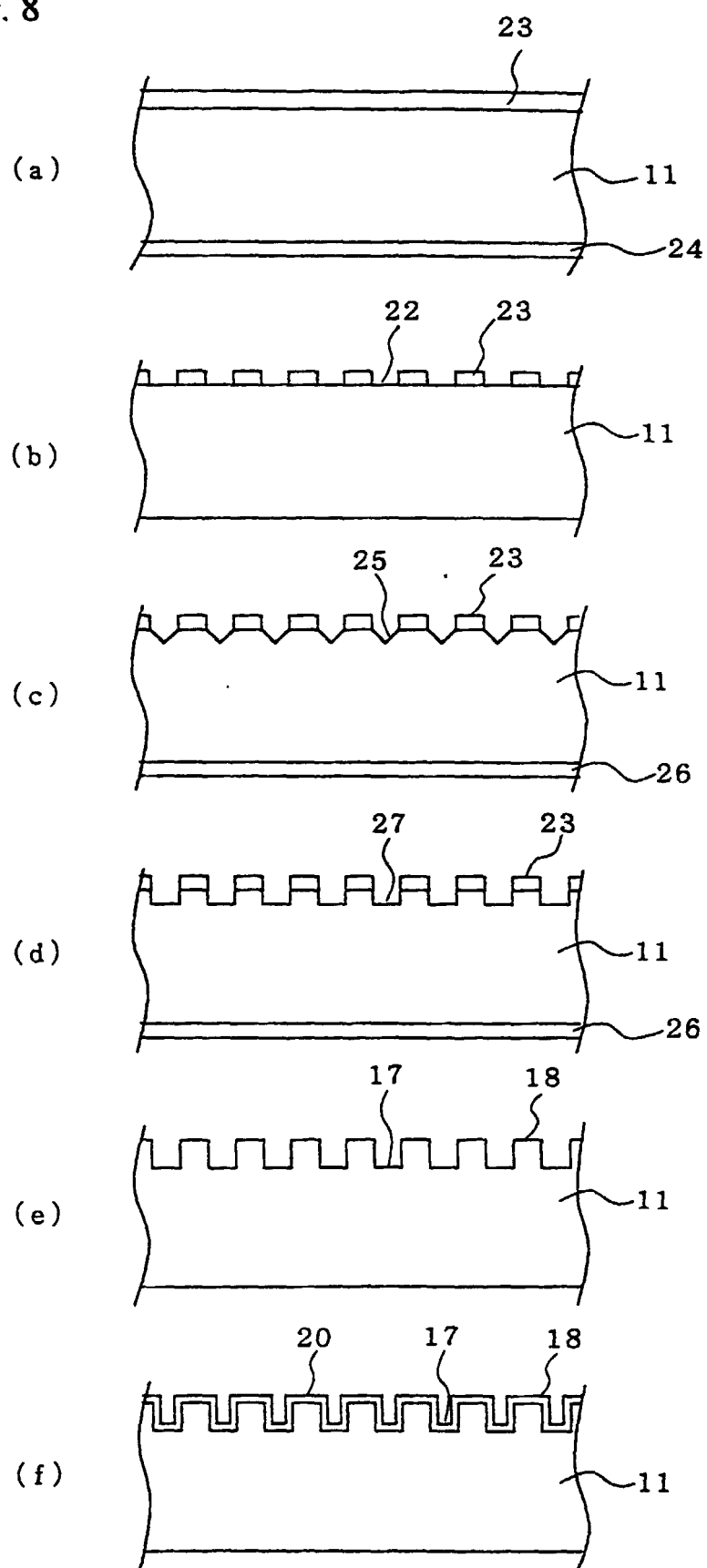


FIG. 9

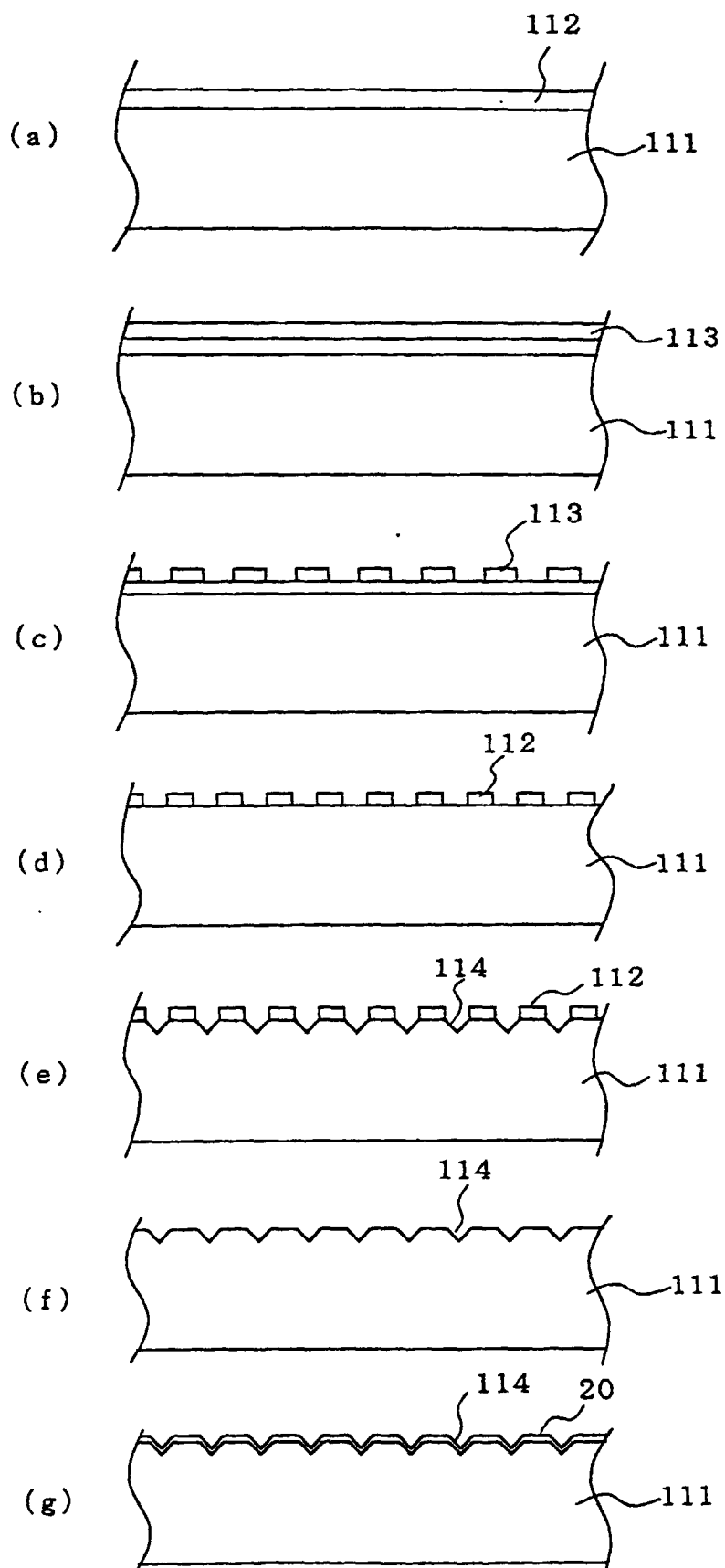


FIG. 10

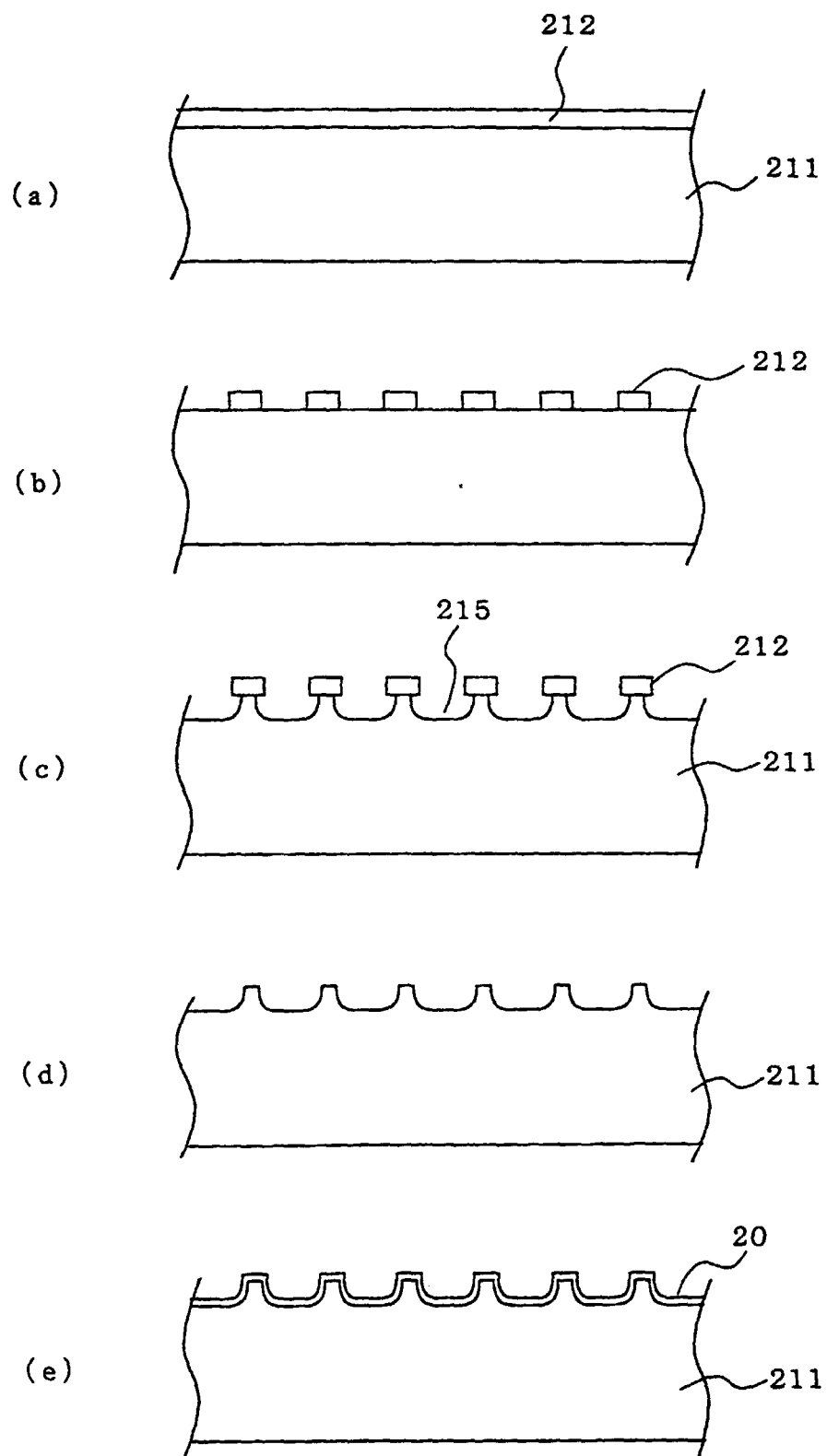


FIG. 11

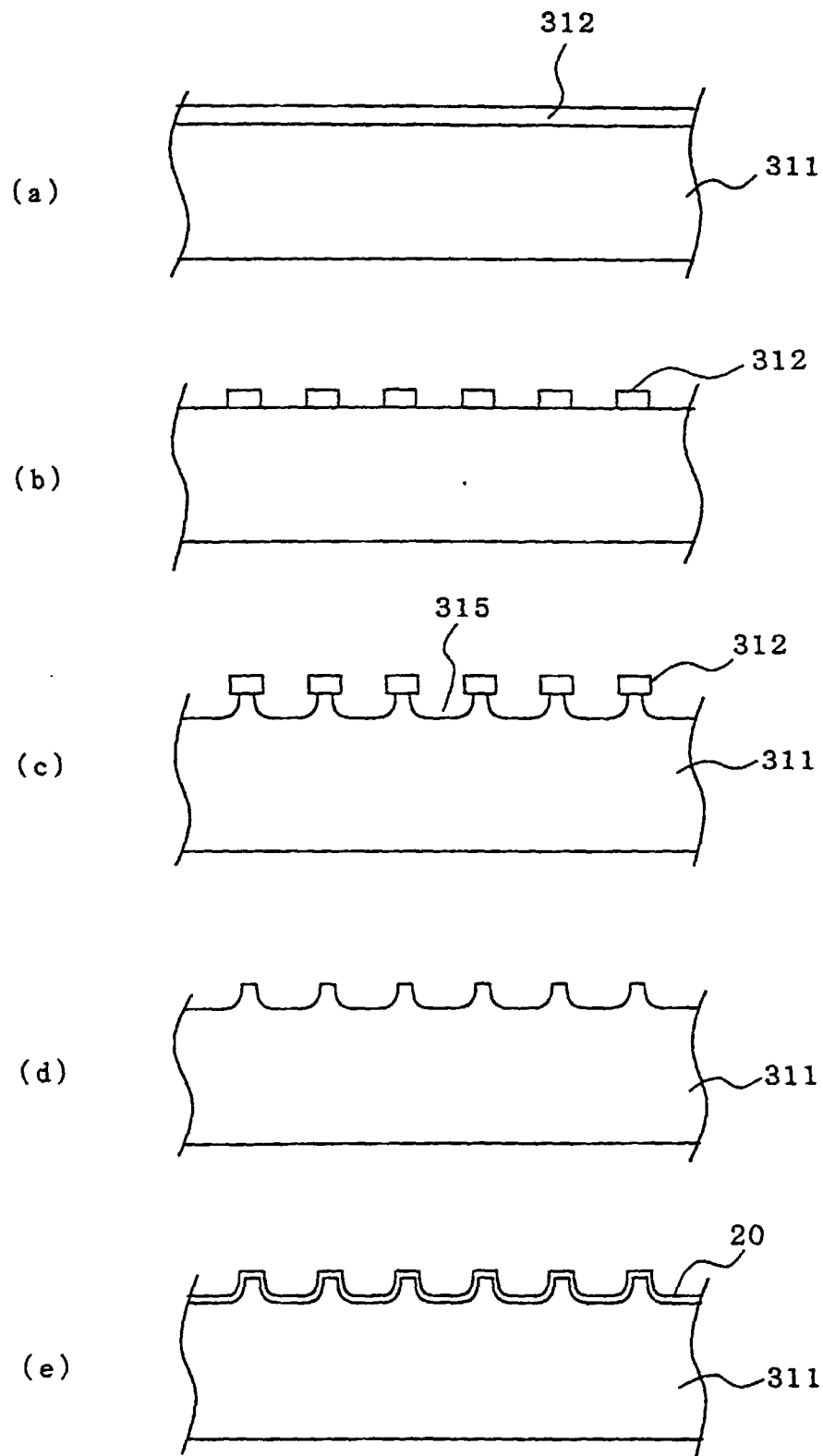


FIG. 12

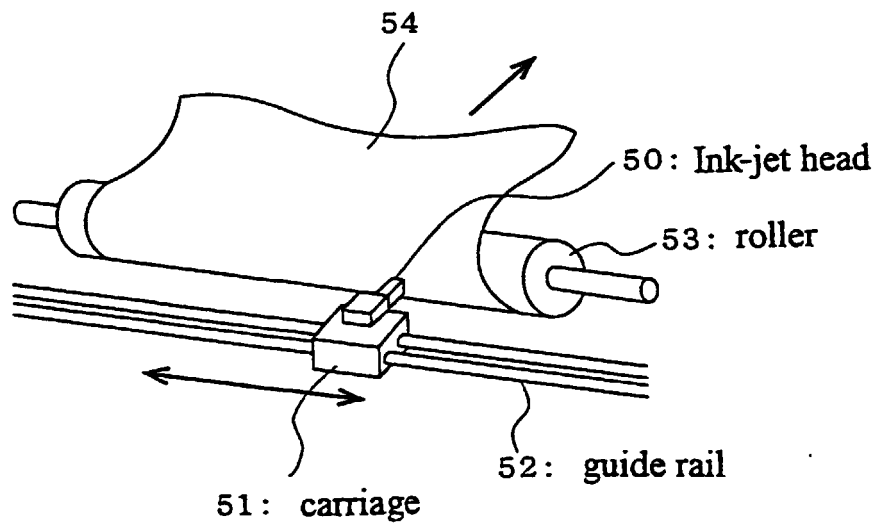


FIG. 13

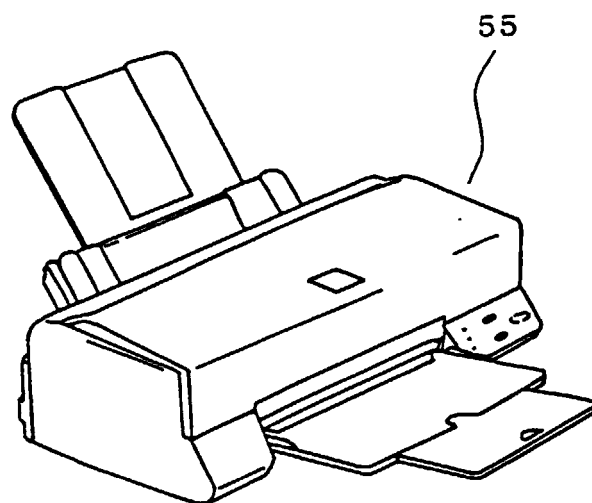




FIG. 14

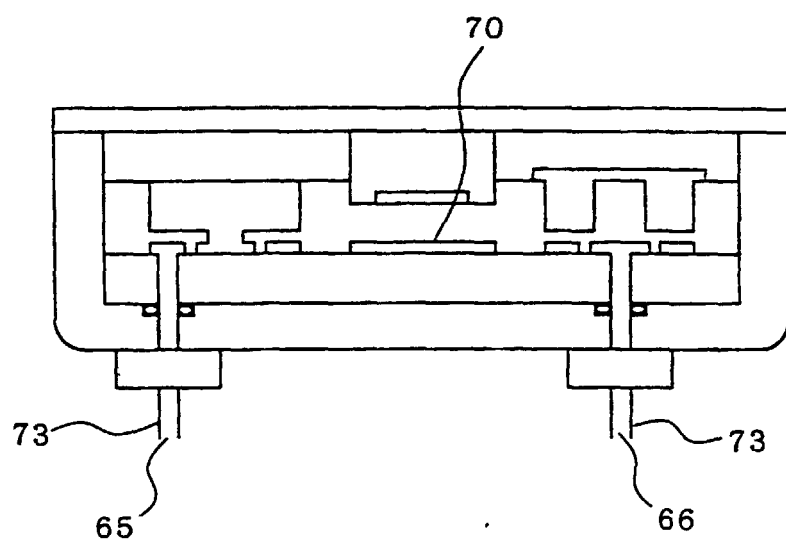


FIG. 15

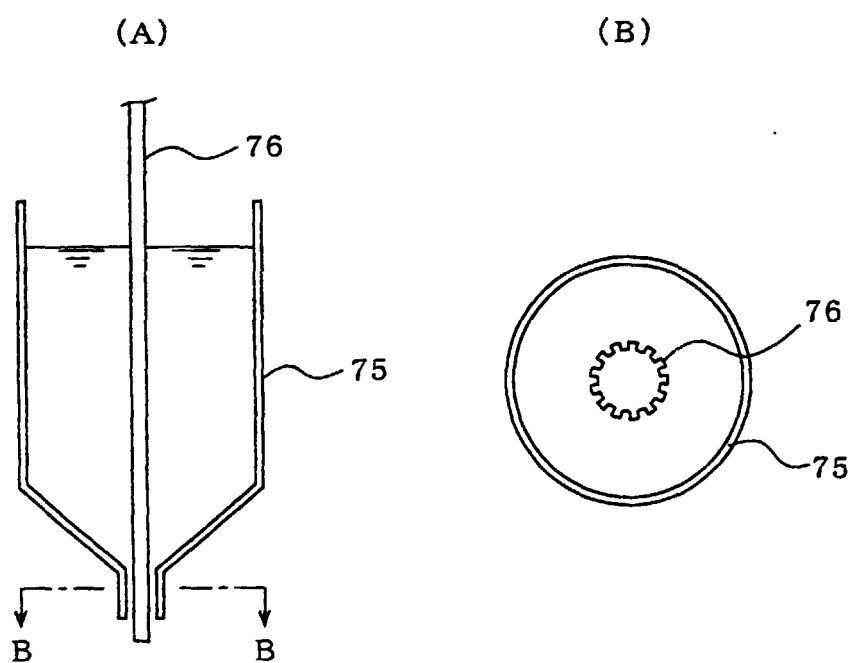


FIG. 16

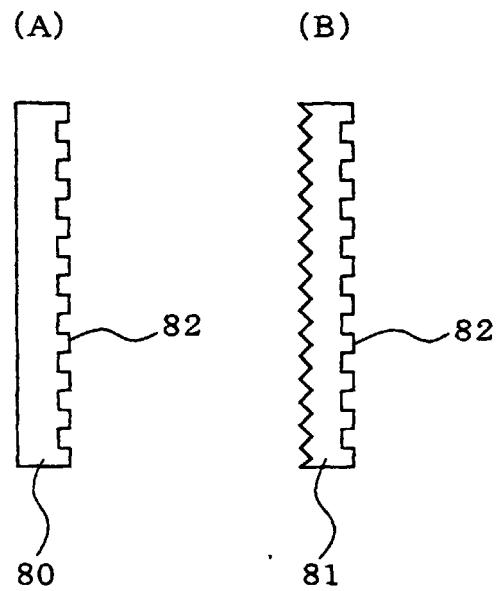


FIG. 17

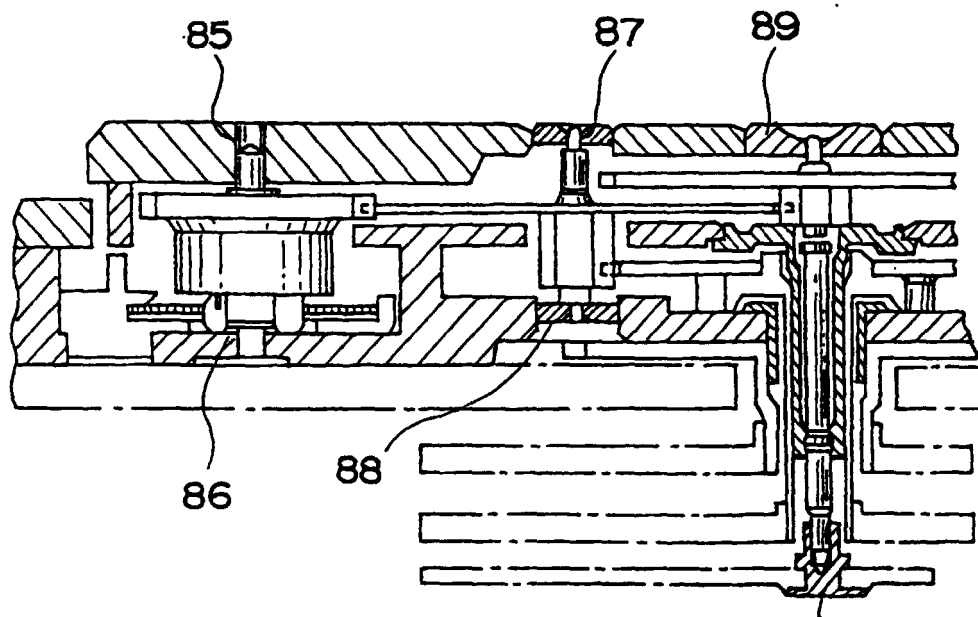
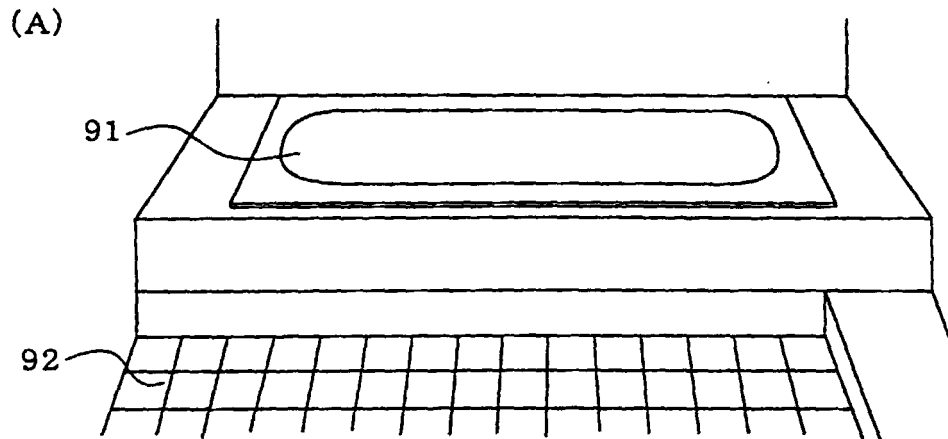
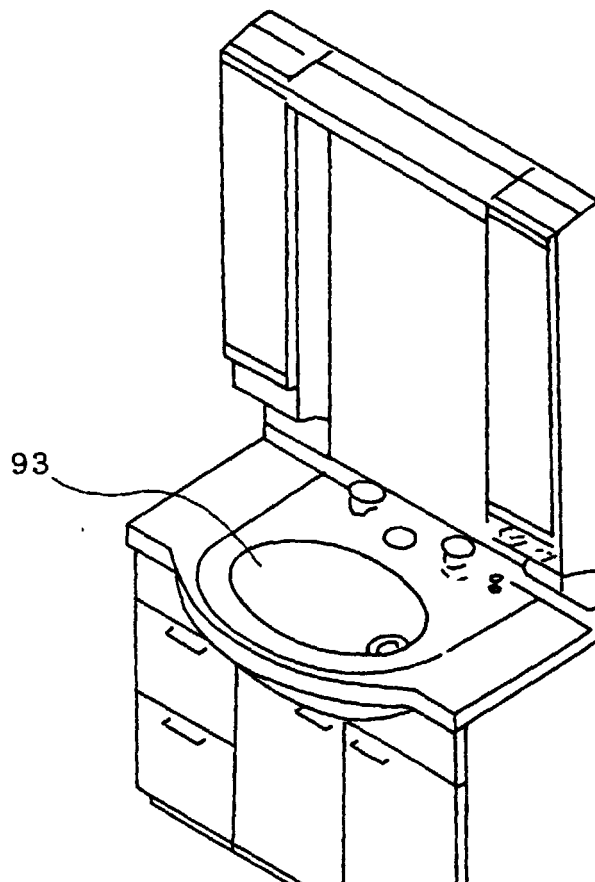


FIG. 18



(B)



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/00870

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>6</sup> B41J2/135		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>6</sup> B41J2/135		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 8-318628, A (Citizen Watch Co., Ltd.),	1-4
Y	3 December, 1996 (03. 12. 96) (Family: none)	7-33
X	JP, 10-157141, A (Canon Inc.),	1-2, 4, 7
Y	16 June, 1998 (16. 06. 98) (Family: none)	7-25
X	JP, 9-278431, A (Central Glass Co., Ltd.),	1-7, 27
	28 October, 1997 (28. 10. 97) (Family: none)	
Y	JP, 5-312153, A (Seiko Epson Corp.),	26, 33
	22 November, 1993 (22. 11. 93) (Family: none)	
Y	JP, 9-331653, A (Tokyo Parts K.K.),	28
	22 December, 1997 (22. 12. 97) (Family: none)	
Y	JP, 8-267646, A (TOTO Ltd.),	29-31
	15 October, 1996 (15. 10. 96) (Family: none)	
Y	JP, 59-4897, A (Matsushita Electric Industrial Co., Ltd.),	32
	11 January, 1984 (11. 01. 84) (Family: none)	
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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 "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 16 March, 1999 (16. 03. 99)		Date of mailing of the international search report 23 March, 1999 (23. 03. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)