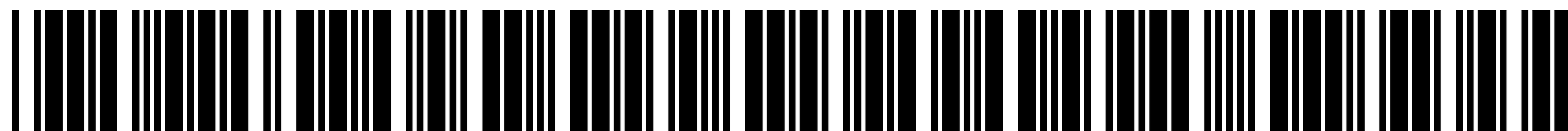

US 20080196834A1

(19) United States

(12) Patent Application Publication

Mizuno et al.

(10) Pub. No.: US 2008/0196834 A1

(43) Pub. Date: Aug. 21, 2008

(54) **LIQUID PHASE ETCHING METHOD AND LIQUID PHASE ETCHING APPARATUS**

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(21) Appl. No.: **12/109,623**

(22) Filed: **Apr. 25, 2008**

Related U.S. Application Data

(62) Division of application No. 10/546,015, filed on Aug. 18, 2005, now Pat. No. 7,378,031, filed as application No. PCT/JP2004/002073 on Feb. 23, 2004.

(30) **Foreign Application Priority Data**

Feb. 21, 2003 (JP) 2003-044550

Publication Classification

(51) **Int. Cl.**
H01L 21/306 (2006.01)

(52) **U.S. Cl.** **156/345.21**

(57) **ABSTRACT**

A liquid phase etching method which comprises spraying a chemically reactive liquid, with a specific speed, to a solid article, an aggregate of solid articles or a gelatinous material to be treated; and a liquid etching apparatus having a mechanism for holding a processing object to be treated and a nozzle structure for spraying a chemically reactive liquid to the processing object to be treated which is held by the mechanism. The method and apparatus allow the significant improvement of the etching rate while maintaining the accuracy of etching.

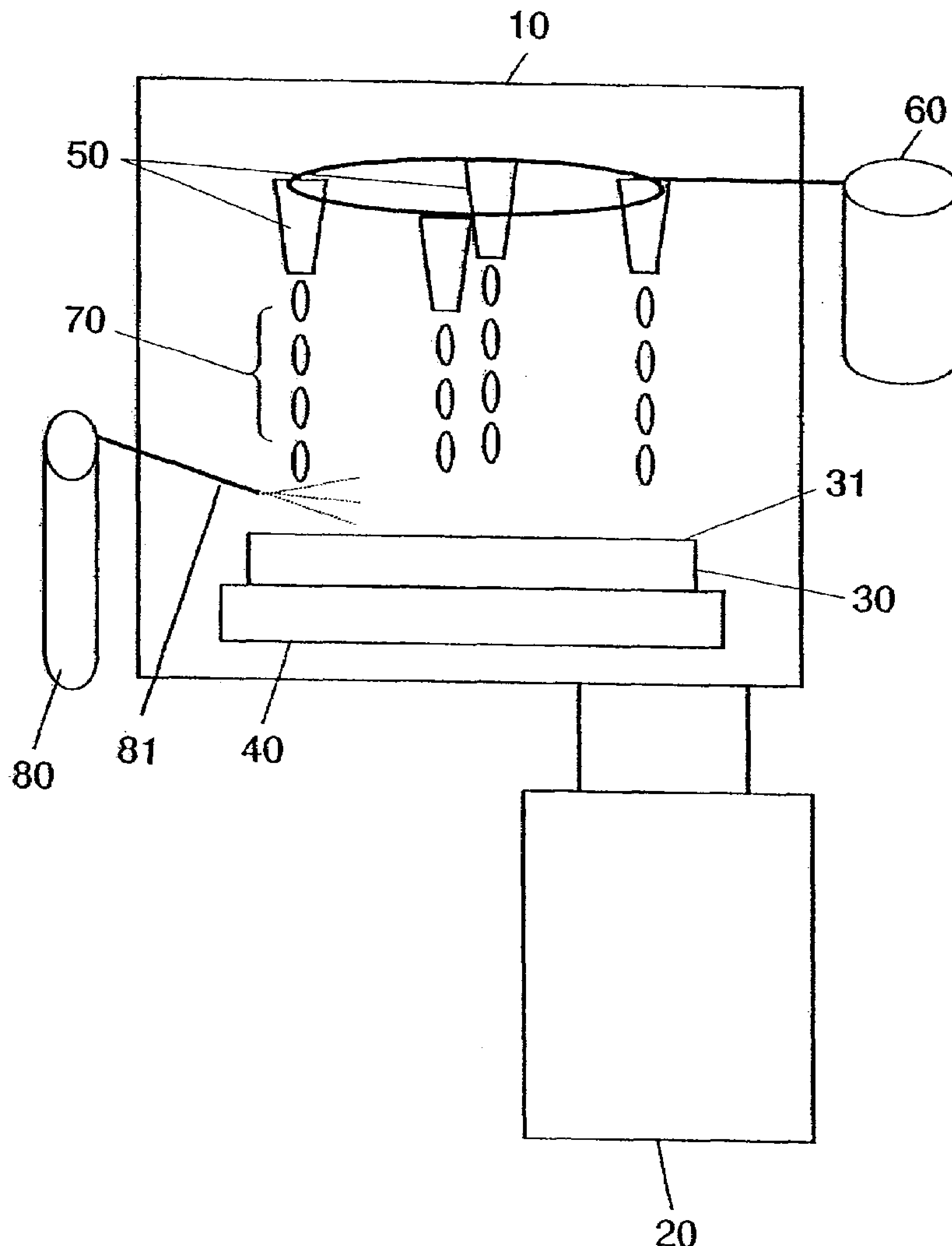


FIG. 1

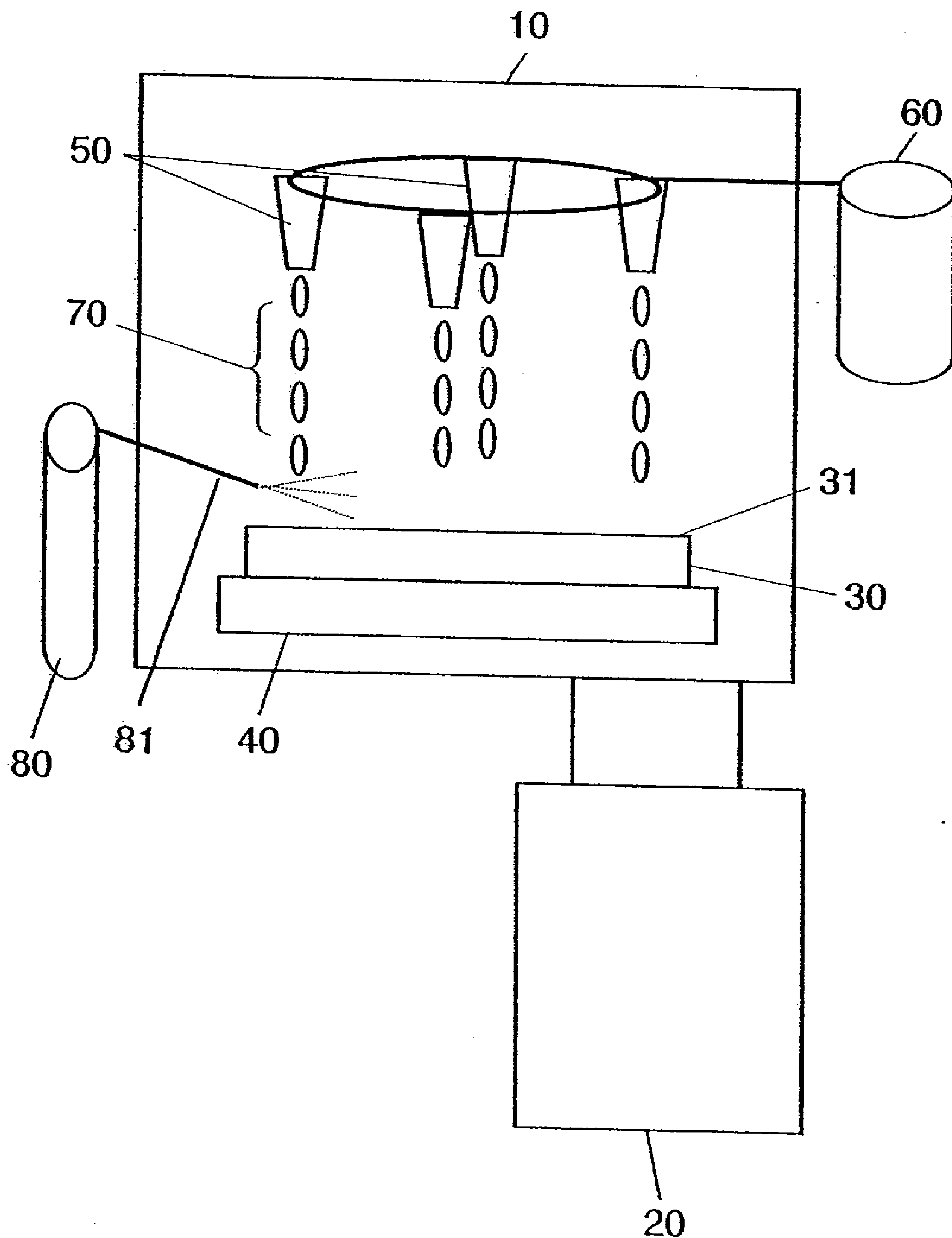


FIG. 2A

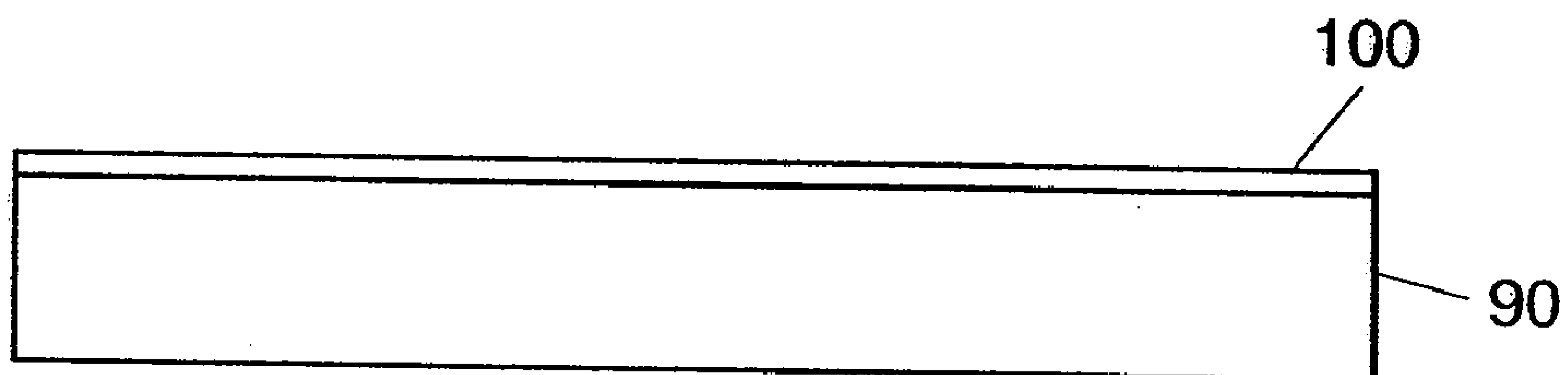


FIG. 2B

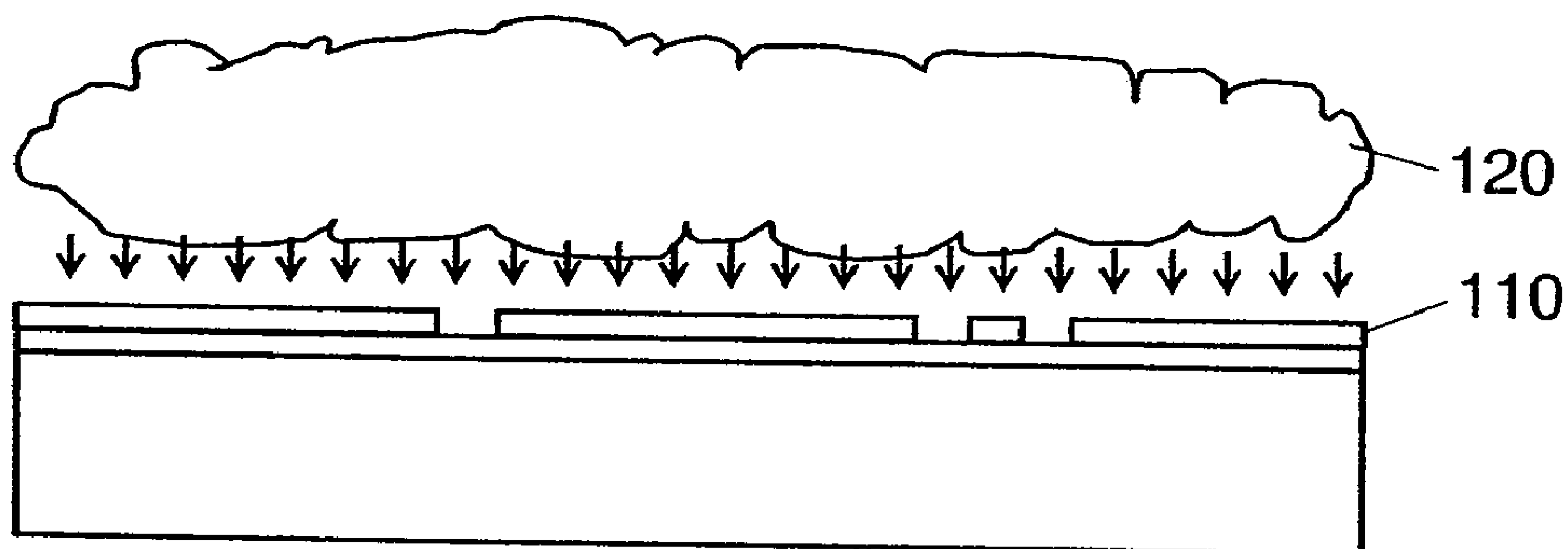


FIG. 2C

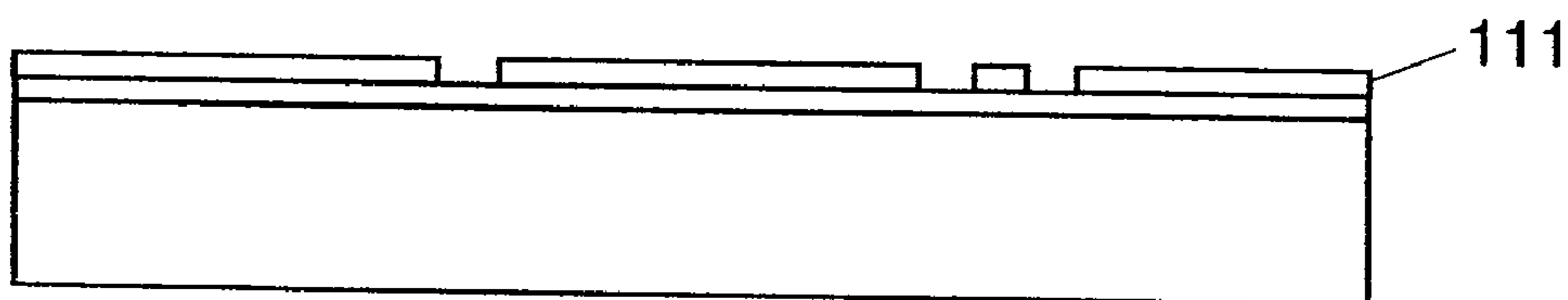


FIG. 2D

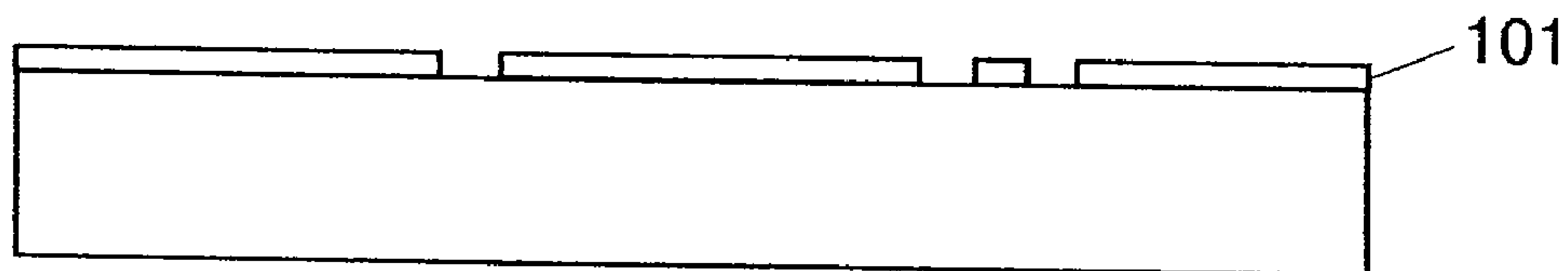


FIG. 3A

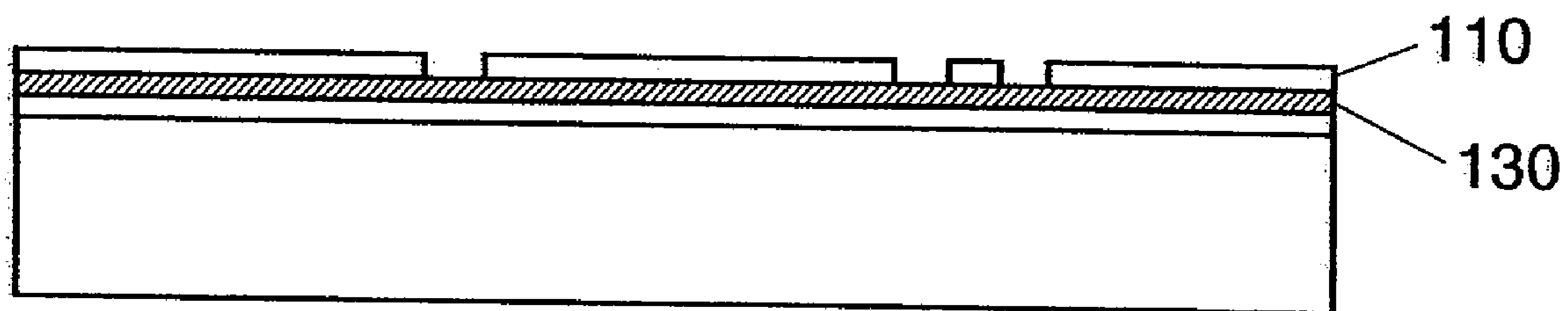


FIG. 3B

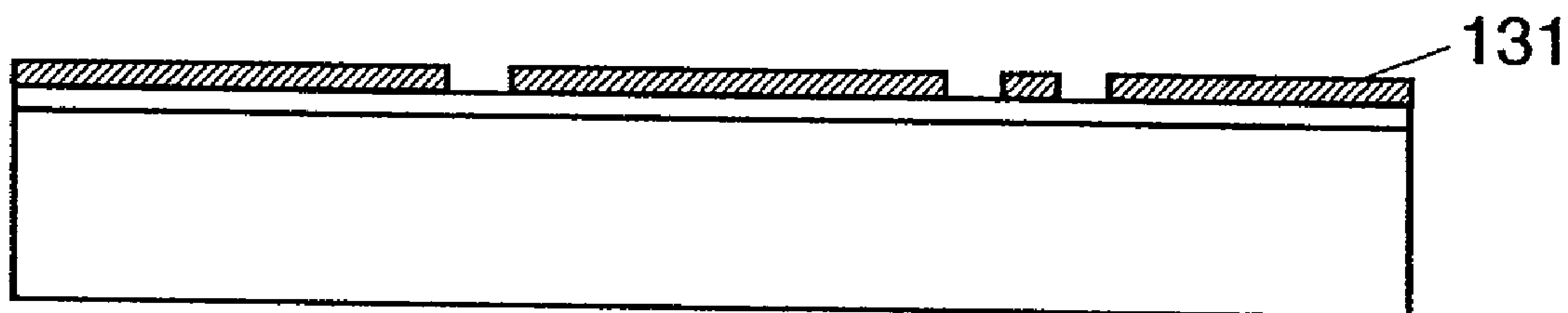


FIG. 3C

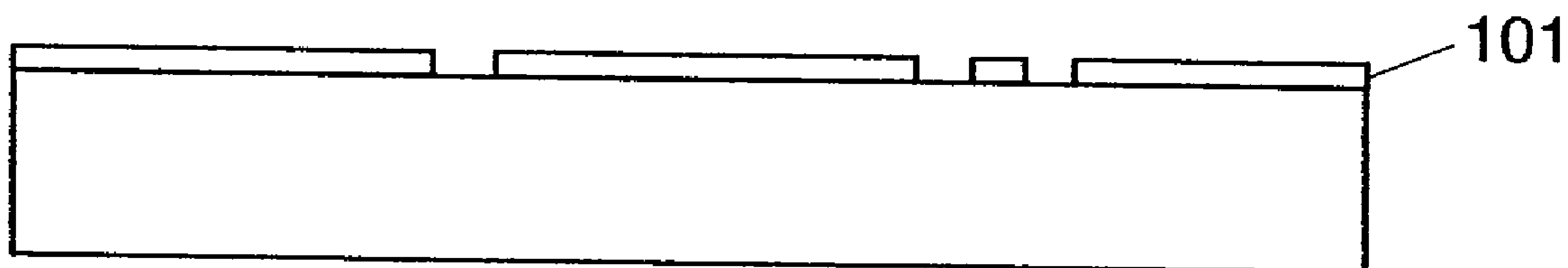


FIG. 4

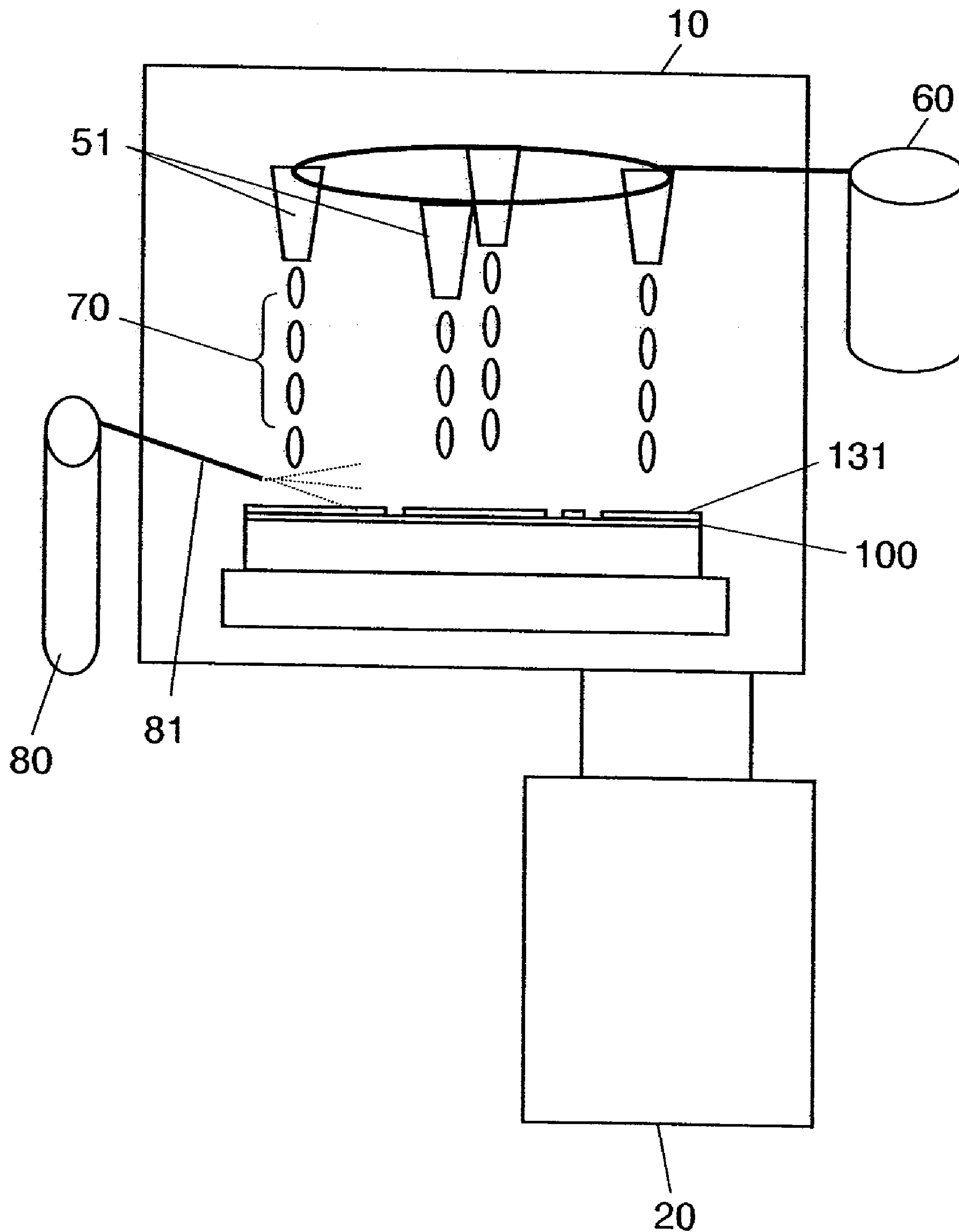


FIG. 5

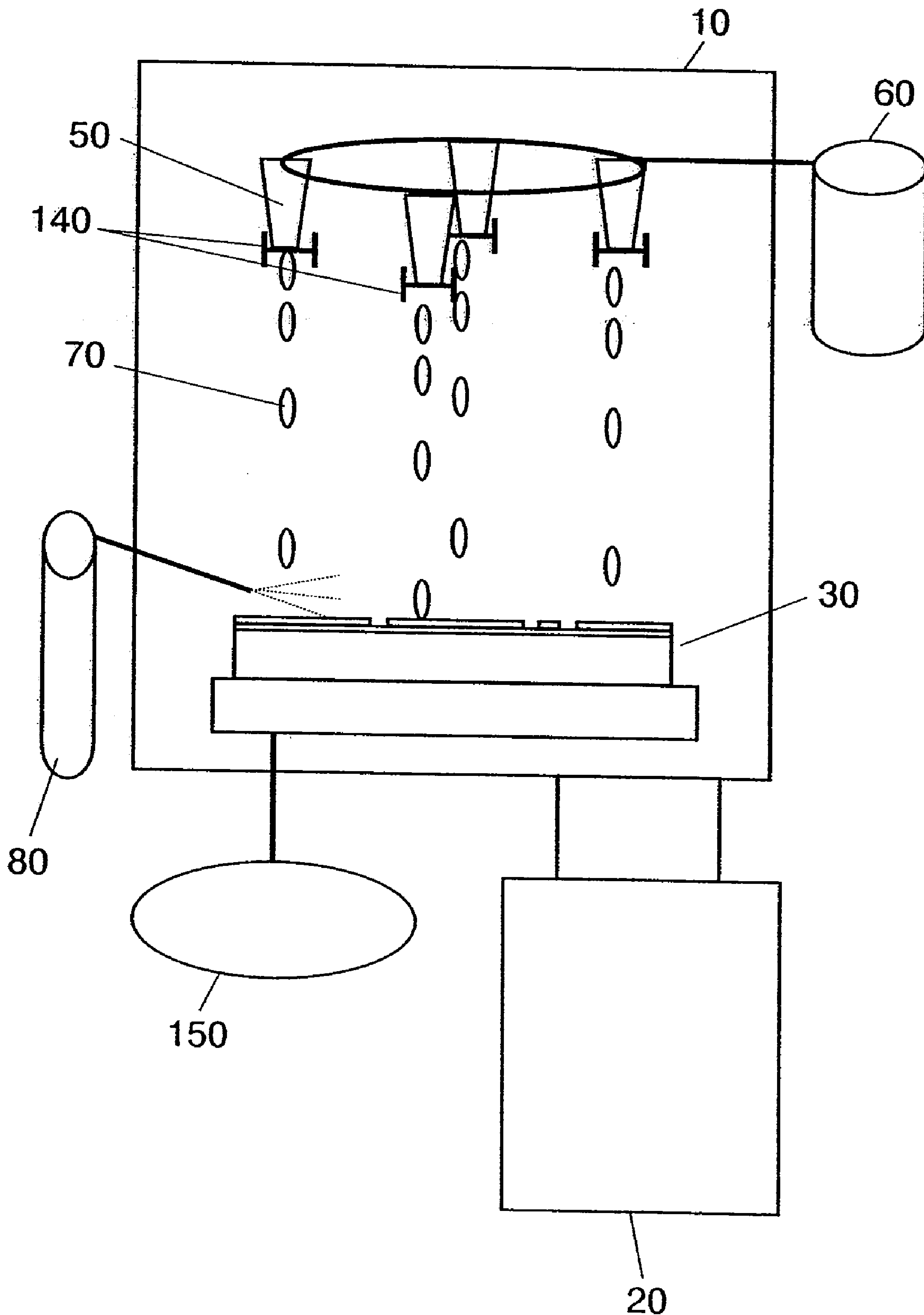


FIG. 6

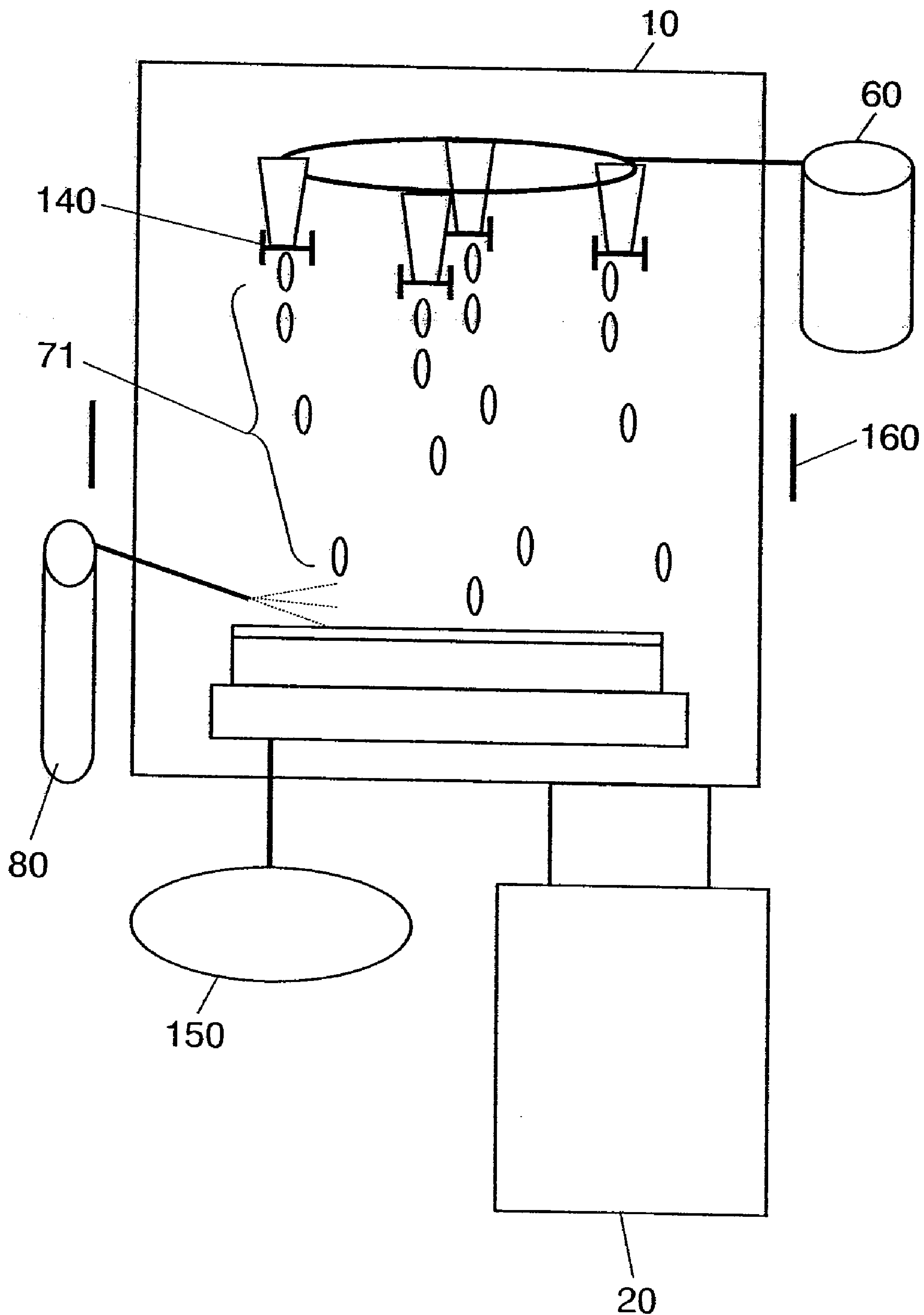


FIG. 7

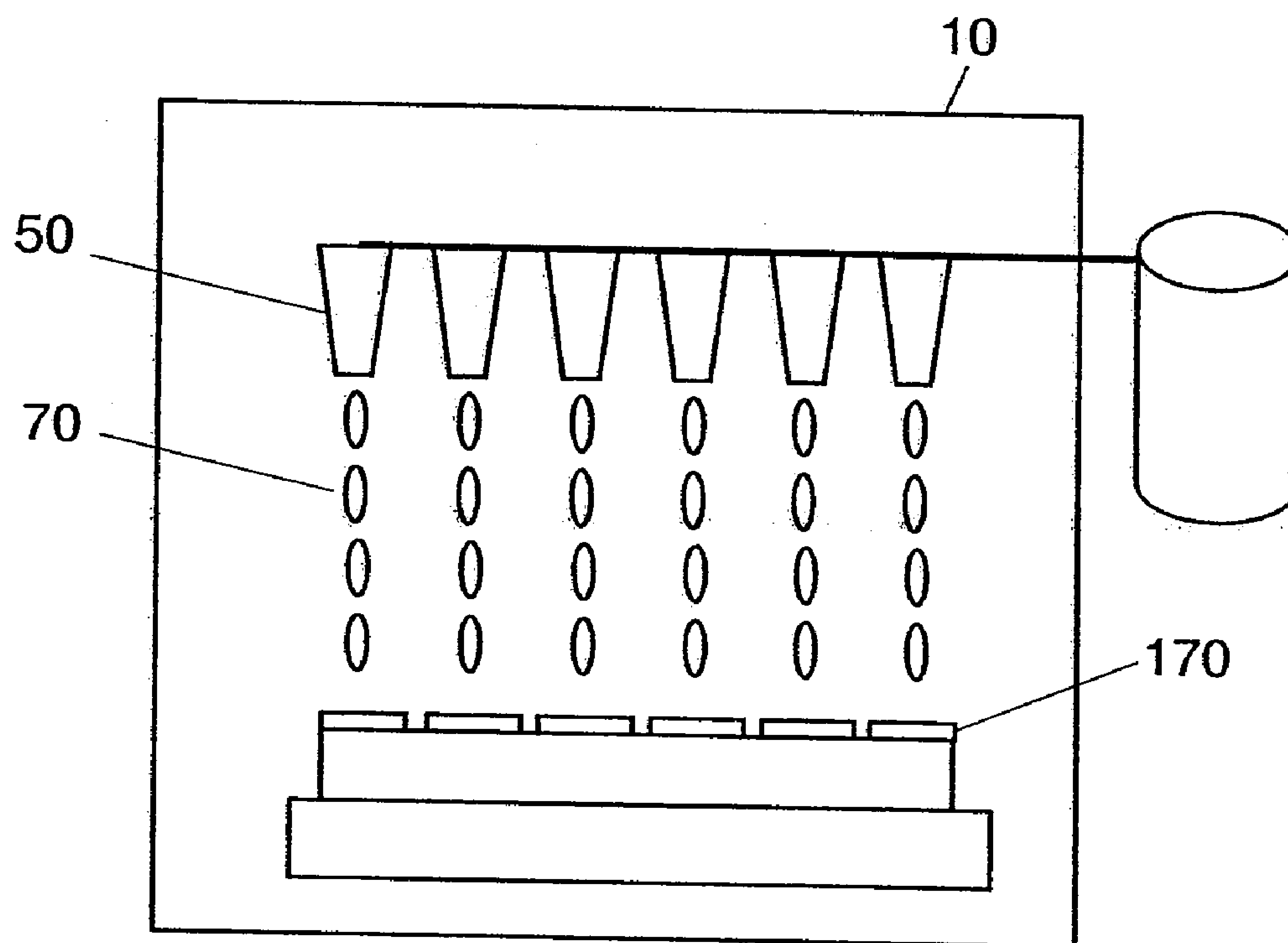


FIG. 8

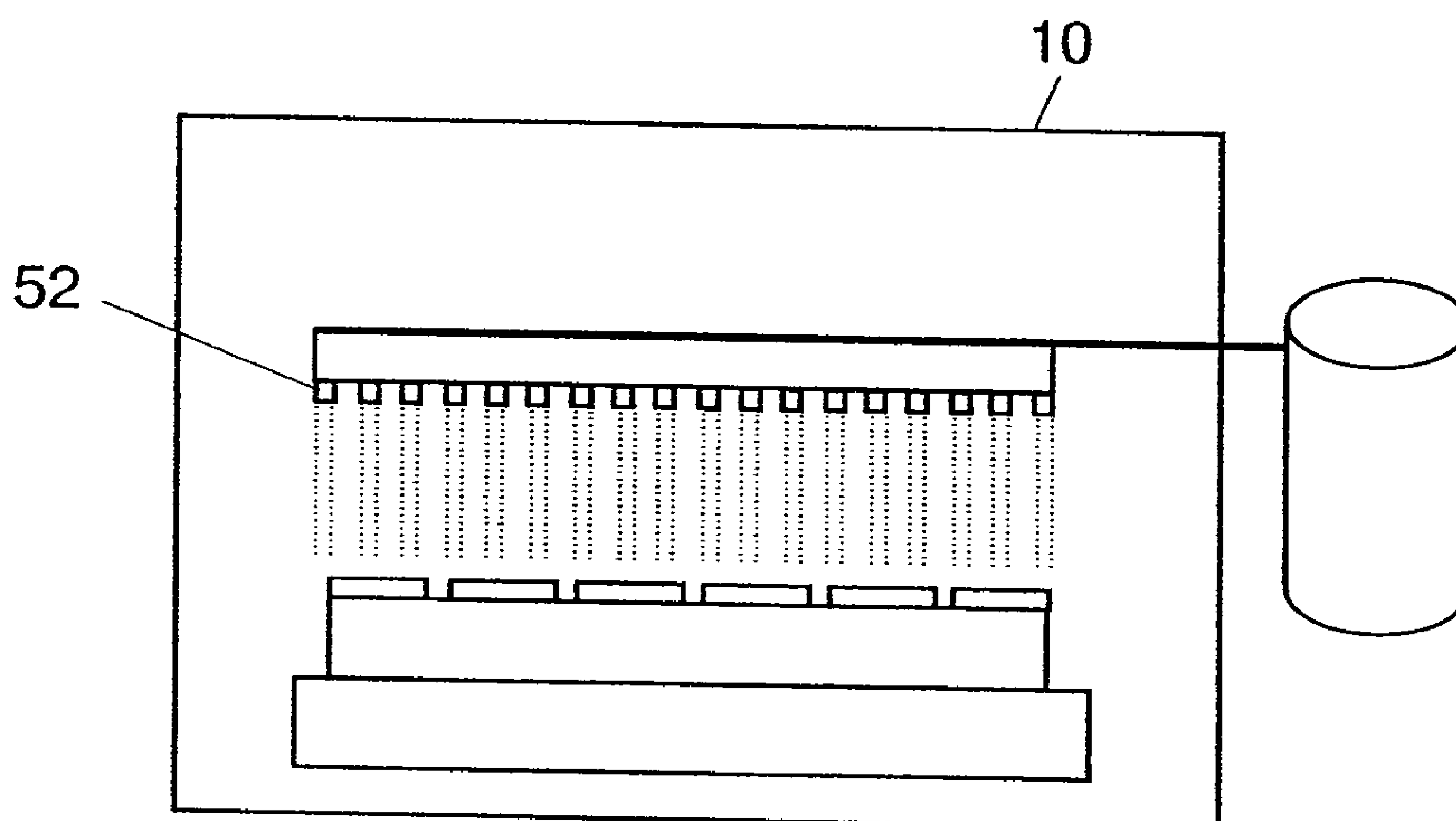
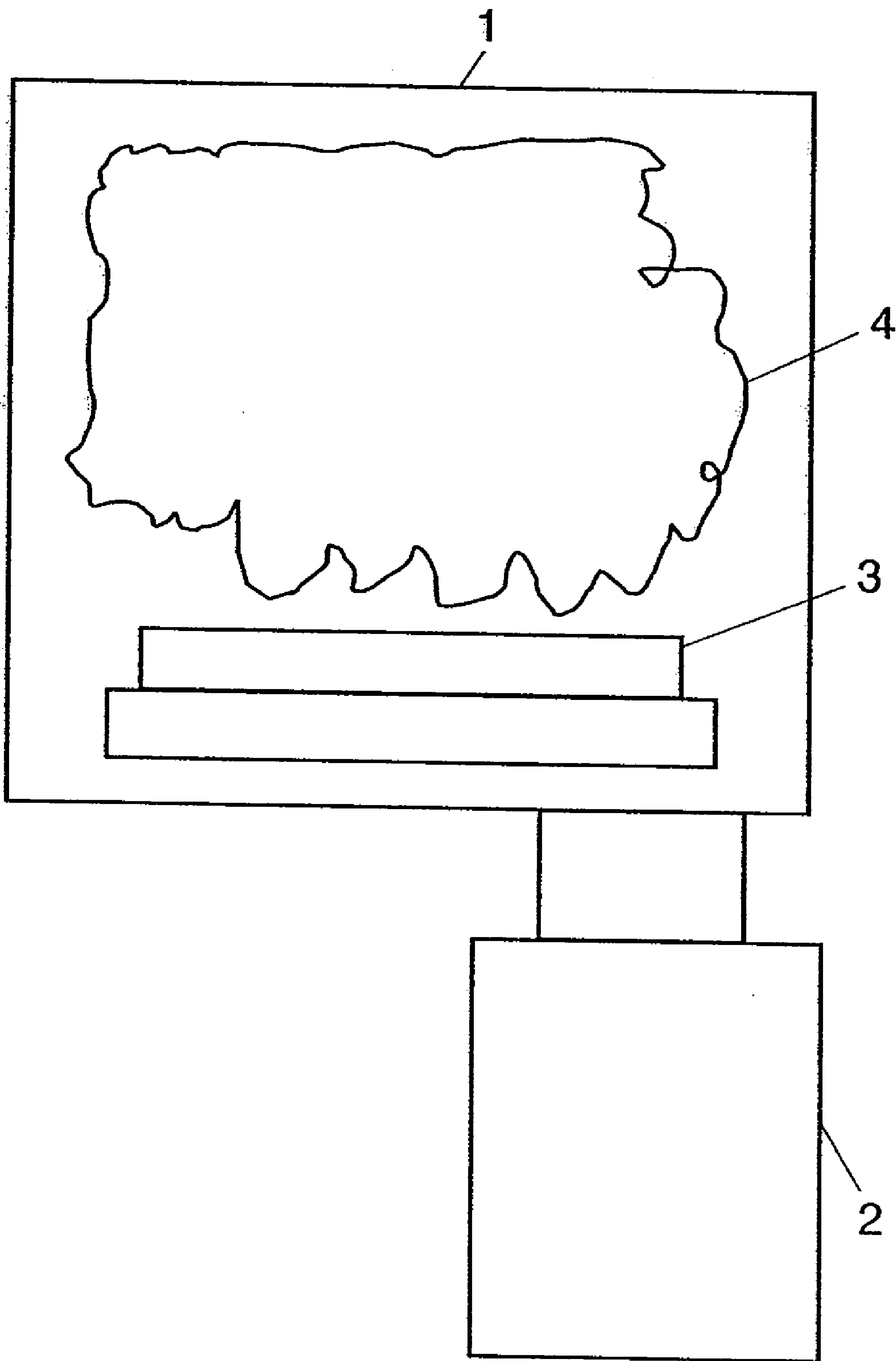


FIG. 9



LIQUID PHASE ETCHING METHOD AND LIQUID PHASE ETCHING APPARATUS

[0001] This application is a divisional of U.S. patent application Ser. No. 10/546,015, filed Aug. 18, 2005, which is a National Phase of PCT/JP2004/002073, filed on Feb. 23, 2004, all of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to a technical field of processing the surface of solid materials or other processing objects, in particular a field of forming fine pattern on them. The field includes, for example, a liquid phase etching method and a liquid phase etching apparatus for use in manufacture of semiconductor device or MEMS (micro-electro-mechanical system) device.

BACKGROUND ART

[0003] In processing (etching) process of semiconductor as a typical example of fine patterning, the semiconductor surface is irradiated with reactive gas in plasma state, and the semiconductor is processed into desired shape.

[0004] Explaining briefly by referring to FIG. **9**, a vacuum chamber **1** is coupled to a vacuum pump **2** for creating vacuum. A processing object like silicon wafer **3** is placed in the vacuum chamber **1**, and desired gas is introduced, and plasma **4** is generated to cause interaction with the surface of the processing object, and the processing object is processed. In FIG. **9**, the processing object is etched.

[0005] Meanwhile, as disclosed in Japanese Patent Unexamined Publication No. H9-27654, the conventional etching was often processed by immersing the solid processing object in liquid. However, etching in the liquid is sufficiently fast in etching processing speed, but is not suited to fine patterning because etching tends to be isotropic.

[0006] The reason of using plasma in etching is to make etching anisotropic in order to meet the demand for higher precision in fine patterning.

[0007] However, when plasma is used in etching, the processing speed is sacrificed. As a result, in the semiconductor industrial field, typically, it took about 10 minutes to process one wafer.

DISCLOSURE OF THE INVENTION

[0008] The etching method of the invention is etching a processing object which may be either solid, solid assembly or gel material, by spraying a chemically reactive liquid at a specified speed.

[0009] Also, the etching method of the invention is spraying a chemically reactive liquid to a processing object placed in a vacuum chamber, by using a nozzle mechanism. The degree of vacuum in the vacuum chamber while processing the processing object may be a sufficient degree of vacuum for preventing generation of impulse wave when surpassing the sonic speed at the time of jet injection of liquid.

[0010] Also, the etching method of the invention is further characterized by impinging the liquid particles charged on the surface to the processing object, which is either solid, solid assembly or gel material, with induced acceleration and induced deceleration in electric field or magnetic field, by applying an electric charge to injected liquid particles.

[0011] Also, the etching method of the invention is further characterized by processing the solid or solid assembly selectively by spraying chemically reactive liquid to the portion exposed from the mask, by covering part of the surface of solid or solid assembly with a resin material and using as mask.

[0012] Also, the etching apparatus of the invention is comprising a mechanism for holding a processing object and a nozzle structure for spraying chemically reactive liquid to the held processing object.

[0013] By using the liquid phase etching method and liquid phase etching apparatus of the invention, the etching speed can be enhanced substantially.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. **1** is a schematic sectional view of liquid phase etching apparatus in an embodiment of the invention.

[0015] FIGS. **2**A to **2**D are process charts showing other processing process in the embodiment of the invention.

[0016] FIGS. **3**A to **3**C are process charts showing other processing process in the embodiment of the invention.

[0017] FIG. **4** is a schematic sectional view of liquid phase etching apparatus in the embodiment of the invention.

[0018] FIG. **5** is a schematic sectional view of another liquid phase etching apparatus in the embodiment of the invention.

[0019] FIG. **6** is a schematic sectional view of another liquid phase etching apparatus in the embodiment of the invention.

[0020] FIG. **7** is a schematic sectional view of a different liquid phase etching apparatus in the embodiment of the invention.

[0021] FIG. **8** is a schematic sectional view of a further liquid phase etching apparatus in the embodiment of the invention.

[0022] FIG. **9** is a schematic sectional view of plasma etching apparatus in a prior art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] The invention is intended to realize both characteristics of (1) high speed etching by using liquid and (2) anisotropic etching by using plasma, simultaneously by spraying liquid to the processing object at an extremely high speed, and hence presents a processing technology capable of processing at high speed and having an extremely sharp anisotropy.

[0024] The system capable of impinging liquid drops at super high speed also has an effect of generating plasma on the top surface of the processing object when the liquid drops impinge, so that the features of the invention may be exhibited more outstandingly.

[0025] The invention enables to transfer the existing "etching process" using plasma to processing in liquid, which is high in processing capability, and hence the productivity is improved from several times to one digit higher. The semiconductor industry requires a tremendous investment for manufacturing equipment. It is extremely difficult to realize the chip unit price worthy of investment, and it is very difficult to adapt to so-called silicon cycle. Therefore, if the etching process time can be improved by one digit, the productivity is enhanced and it is expected to change the industrial structure dramatically.

[0026] A preferred embodiment of the invention is described below while referring to the accompanying drawings. In the drawings, the components having same basic function are identified with same reference numerals.

Preferred Embodiment

[0027] A preferred embodiment of the invention is explained by referring to embodiment 1. FIG. **1** is an explanatory diagram of liquid phase etching apparatus used in the preferred embodiment. Referring now to FIG. **1**, the outline of the etching apparatus of embodiment 1 is explained. A vacuum chamber **10** is coupled to a vacuum pump **20** for creating vacuum. A stage **40** and plural nozzles **50** are placed in the vacuum chamber **10**. The stage **40** holds a processing object **30** which is either solid, solid assembly or gel material. The nozzles **50** are connected to a liquid feed device **60** for feeding specified liquid, and particles of chemically reactive liquid **70** can be sprayed to the processing object **30**. From a variety of liquid **70** capable of etching the processing object **30**, a solvent suited to the processing object is selected and used.

[0028] Keeping the vacuum chamber at a higher degree of vacuum than about 1E-3 Torr (that is, at lower pressure), the liquid **70** is sprayed from the nozzles **50** at a speed of over 1000 km/hour. The sprayed liquid **70** wets the processing object surface **31**, which is etched simultaneously.

[0029] If wettability of liquid **70** on the processing object surface **31** is poor, a surface active agent is sprayed to the processing object surface from a spray outlet **81** of a surface active agent feed device **80**. The surface active agent may be sprayed before spraying of liquid **70**, simultaneously with spraying, or right after spraying of liquid **70**. By the presence of surface active agent, the liquid **70** permeates into all parts of the processing object surface **31**, and it is etched uniformly.

[0030] For example, when the liquid **70** is sprayed to the processing object **30** by accelerating to a speed of more than 10,000 km/hour, part of liquid components may be transformed into plasma by gaining a high energy. The generated plasma is effective to activate the processing object surface **31**, and further accelerate the etching process speed.

[0031] Anticorrosive processing of nozzles **50** is explained.

[0032] Nozzles are not always made of materials excellent in corrosion resistance. If nozzles are made of materials not so high in corrosion resistance, the nozzle basic shape is formed by using a material suited to nozzle processing, and the surface directly contacting with the etching liquid must be coated with an anticorrosive substance. This coating process is either irradiation of nozzle surface directly with plasma mainly composed of desired anticorrosive substance, or irradiation of nozzle surface with plasma for generating an anticorrosive substance by reacting with the material forming the basic shape. Coating the nozzle surface with an anticorrosive substance enables the corrosion resistance of the nozzle to the etching liquid to improve remarkably.

[0033] Other processing process of the preferred embodiment of the invention is explained by referring to embodiment 2. FIGS. **2**A to **2**D, FIGS. **3**A to **3**C and FIG. **4** explain embodiment 2. FIGS. **2**A to **2**D are process charts of embodiment 2 showing the process in the case of using the photo resist as mask and semiconductor as processing object. FIGS. **3**A to **3**D are process charts of embodiment 2 showing the process in the case of using the coating substance as mask and semiconductor as processing object. And FIG. **4** is an explanatory diagram of etching apparatus of embodiment 2 in the case of using semiconductor as processing object.

[0034] As an example of fine patterning of processing object **30**, the latest processing of fine patterning of semiconductor device is explained.

[0035] In 2002, generally, the semiconductor is processed more finely than 0.25 μm. Accordingly, the size of fine particles of liquid **70** for processing it should be smaller than 0.2 μm. The size of fine particles may be small enough for the factor determining the size of the object of processing (critical dimension). If the required processing precision is large, the size of a corresponding particle may be selected from sizes smaller than the required processing precision. In embodiment 2, the etching apparatus includes nozzles **50** for forming fine particles smaller than 0.2 μm, or supersonic nozzles **51** for forming liquid fine particles at higher speed. In the invention, the supersonic nozzles spray liquid fine particles at a speed of no less than 1000 km/hour, or more preferably spray liquid fine particles by accelerating to a speed of no less than 3,000 km/hour.

[0036] Referring to FIG. **2**, the semiconductor substrate to be processed is explained. As an example of semiconductor substrate, a silicon wafer **90** forming a thin film **100** of a substance necessary for forming a semiconductor element thereon is used. The semiconductor substrate to be processed is silicon substrate, or silicon substrate forming silicon oxide film, silicon nitride film, oxide film of rare earth elements, or metal film of aluminum or copper, thereon.

[0037] Although there are various liquid for etching the thin film **100** of processing object material, a solvent suitable for the material of the semiconductor substrate to be processed is selected and used.

[0038] The degree of vacuum of vacuum chamber **10** is kept higher than about 1E-3 Torr, and the liquid **70** is sprayed from the nozzles **50** at a speed of no less than about 1000 km/hour. When the sprayed liquid reaches and wets the processing object surface **31**, it is etched at the same time. Depending on a relation between processing object surface **31** and liquid **70**, a surface active agent is used for the liquid permeating into all parts of the processing object surface **31**, and for obtaining a homogeneous etching effect. If wetting of liquid **70** on the processing object surface **31** is poor, by spraying the surface active agent to the processing object surface, the liquid **70** is distributed in all parts of the processing object surface **31**, so that uniform etching is attained.

[0039] For example, if the liquid **70** reaches the processing object at a high speed exceeding about 10,000 km/hour, part of liquid components may be transformed into plasma by receiving high energy. The generated plasma activates the processing object surface, and may further accelerate the etching speed.

[0040] When manufacturing a semiconductor device, it may be required to process in a very fine size of 0.1 μm smaller than 0.25 μm. In such a case, as shown in FIG. **2**B, a photo resist **110** is formed on the thin film **100**, using it as mask, it may be processed in desired pattern and size by using the so-called lithography. At this time, in order to provide the photo resist with corrosion resistance to withstand liquid phase etching, it is preferred to process the surface of photo resist **110** preliminarily by plasma **120** as shown in FIG. **2**B.

[0041] By plasma processing of the surface of the photo resist composed of organic materials, polymerization reaction of organic materials takes place on the surface. By this reaction, cross linking of organic materials on the surface is

promoted, so that an anticorrosive photo resist **111** obtained as shown in FIG. **2**C. An appropriate plasma **120** may be determined in consideration of: plasma of rare gases; interaction with substance for composing the photo resist **110**; interaction with etching liquid **70** such as solvents, acid or alkali to be used.

[0042] Depending on the combination of etching liquid **70** such as solvents, acid or alkali to be used, sufficient corrosion resistance may not be achieved in the photo resist **110** mainly composed of organic materials.

[0043] In such a case, as shown in FIG. **3**, a coating substance **130** made of material having enough corrosion resistance is applied on the surface of the processing object **100**, and liquid phase etching is executed by using the coating substance **130** as mask. In embodiment 2, the processing object corresponds to the thin film **100** formed on the surface of silicon substrate **90**.

[0044] At first, using the photo resist **110** as mask, the coating substance **130** is etched by using etching liquid **70**, such as solvent, acid or alkali, capable of etching the coating substance **130**.

[0045] Further, using the patterned coating substance **131** as mask, as shown in FIG. **4**, in the vacuum chamber **10**, the processing object **100** is etched in liquid phase and processed as desired by spraying the solvent and acidic or alkaline etching liquid **70** for etching the processing object **100** from the supersonic nozzles **51**. The vacuum degree in the vacuum chamber **10** is kept at degree of vacuum higher than 1E-3 Torr (that is, lower pressure), and the liquid **70** is sprayed from nozzles **51** at a speed of higher than 1,000 km/hour. The degree of vacuum is thus maintained in order to prevent generation of impulse waves or the like by surpassing the sonic speed at the time of jet injection of the chemically reactive liquid.

[0046] By the method explained above, the semiconductor substrate or other thin film to be processed can be processed very finely according to the mask pattern.

[0047] Other processing process of the preferred embodiment of the invention is explained below by referring to embodiment 3. In manufacture of semiconductor device in which precision processing is required, overhang of etching groove or forming of taper may cause to worsen the processing precision. Hence, there is a strong demand for an etching method of digging groove in the vertical direction from the surface of flat solid body.

[0048] Embodiment 3, by referring to FIG. **5** and FIG. **6**, explains an etching method of digging groove in the vertical direction by making use of electric field or magnetic field at the time of etching process.

[0049] FIG. **5** is an explanatory diagram of etching apparatus for accelerating the liquid **70** by applying an electric field to the processing object in embodiment 3 of the invention, and FIG. **6** is an explanatory diagram of etching apparatus for accelerating the liquid **70** in rotating direction by applying a magnetic field to the vacuum chamber in embodiment 3 of the invention.

[0050] As shown in FIG. **5**, a charging mechanism **140** is provided at the outlet or near the outlet of the nozzles **50**, and an electric charge is applied to the ejecting pulverized liquid (that is, liquid particles) **70**. By making use of this electric charge, the ejecting pulverized liquid **70** is provided with freedom in directivity. For this purpose, a voltage application mechanism **150** is provided for applying a voltage to the stage holding the semiconductor solid.

[0051] The liquid **70** sprayed out from the nozzles **50** is first provided with an electric charge by the charging mechanism **140**, and is accelerated by the voltage application mechanism **150** and reaches the processing object **30**. The applicable voltage is limited by electric discharge or leak varying with the structure of the apparatus or electrical characteristic of the liquid to be used. This problem will be further discussed in embodiment 5. By applying the voltage intermittently by combining with a system of promoting vaporization of the liquid used in the etching, effects of current leak or the like may be prevented.

[0052] Further, as shown in FIG. **6**, by using a magnetic field application mechanism **160** for applying a magnetic field, the liquid **71** can be accelerated in the rotating direction, and the motion trajectory can be varied, and the direction can be controlled freely. Reference numeral **71** refers to the liquid rotated in its trajectory.

[0053] Another processing process of the preferred embodiment of the invention is explained below by referring to embodiment 4. Only one nozzle **50** for injecting liquid may be used in etching process, but when the processing object such as a solid has a certain area, if only one nozzle is used then, the incident angle to the surface of the pulverized liquid particles varies depending on the location of the processing. This is the same phenomenon as a flat surface illuminated by a spot light source varies in luminance depending on the location. Therefore, to process uniformly on the entire surface of the processing object, it is effective to use plural nozzles. In embodiment 4, a case of using the plural nozzles is explained.

[0054] FIG. **7** shows an etching apparatus in embodiment 4 of the invention, in which nozzles are provided at every individual semiconductor chip. FIG. **8** shows an etching apparatus having numerous fine nozzles by making use of MEMS in embodiment 4 of the invention.

[0055] For example, in the manufacturing process of silicon semiconductor, plural chips **170** are formed at intervals of about 1 cm. As shown in FIG. **7**, nozzles **50** are installed immediately above the individual chips **170**, and the angle variation of liquid **70** may be minimized. Besides, by installing the plural nozzles in every chip, effects of angle changes may be minimized.

[0056] Further, as shown in FIG. **8**, for example, by using micro nozzles **52** making use of MEMS or micro machining, nozzles may be disposed at intervals of several microns. At this time, etching may be carried out using nozzles densely installed in an area corresponding to the entire surface of the processing object. Or by installing nozzles in a specific area, and by moving the nozzles or the processing object, the entire surface of the processing object may be etched. In FIG. **8**, each nozzle is shown in magnified view for the sake of explanation.

[0057] A further processing process of the preferred embodiment of the invention is explained below by referring to embodiment 5. Depending on the characteristic of the etching liquid, such as solvent, acid or alkali, used in liquid phase etching, the time of vaporization of the liquid used in the etching in the vacuum chamber **10** varies.

[0058] When the vaporization speed is sufficiently fast, the sprayed liquid is soon vaporized after a specified etching time and there is no problem. If the vaporization speed is slow, the liquid remains after necessary etching time, which may lead to etching defects. Accordingly, when the vaporization speed is slow, it is required to prevent excessive supply of liquid by controlling the spraying amount of the etching liquid. To

solve this problem, the liquid feed device **60** includes an intermittent spray circuit or intermittent spray device (not shown), and the liquid is sprayed from the nozzles intermittently, and it is preferred to set a necessary time interval for allowing the etching liquid to be evaporated after being sprayed out.

[0059] In the foregoing preferred embodiment, it is desired to spray the chemically reactive liquid at super high speed, but if not so high, the speed may be enough as far as part or most of liquid components can be transformed into plasma.

INDUSTRIAL APPLICABILITY

[0060] As explained herein, the invention presents a liquid phase etching method capable of spraying an etching liquid to the processing object at a high speed, and is intended to enhance the etching speed substantially while maintaining anisotropy or other fine patterning performance of dry etching.

1. A liquid phase etching apparatus comprising:
- a vacuum chamber; and
- a nozzle mechanism provided in the vacuum chamber for spraying a chemical reactive liquid to a processing object in vacuum atmosphere,
- wherein at least the nozzle mechanism is protected by anticorrosive treatment, the anticorrosive treatment is a process of forming a thin film of substance having corrosion resistance to the liquid in the exposed part of the nozzle mechanism, and the treatment is a surface treatment by using plasma.

2. The liquid phase etching apparatus of claim **1**, further comprising:
- a stage for holding the processing object,
- a charging mechanism provided at the exit of the nozzle mechanism, and
- a voltage application mechanism for applying a voltage to the stage,
- wherein the charging mechanism applies an electric charge to particles of the sprayed liquid, and
- the voltage application mechanism can accelerate the charged particles of the liquid.

3. The liquid phase etching apparatus of claim **1**, further comprising a magnetic field application mechanism, wherein the magnetic field application mechanism controls the trajectory of liquid particles.

4. The liquid phase etching apparatus of claim **1**, further comprising a liquid feed device, wherein the liquid feed device feeds the liquid continuously or intermittently to the nozzle mechanism.

5. The liquid phase etching apparatus of claim **1**, further comprising a surface active agent feed mechanism, wherein the surface active agent feed mechanism includes:
- a spraying section for spraying the surface active agent to the processing object, and
- a feed device for feeding the surface active agent to the spraying section.

6. The liquid phase etching apparatus of claim **1**, wherein the vacuum atmosphere has higher degree of vacuum than 1E-3 Torr.

* * * * *