

1. X-ray Mask Structure and X-ray Exposing
Method, and Semiconductor Device Manufactured
by Use of X-ray Mask Structure, and Method
for Manufacturing X-ray Mask Structure

5

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an X-ray mask
structure for use in the manufacture of semiconductor
10 devices and the like, an X-ray exposing method by the
use of the X-ray mask structure, a semiconductor device
manufactured by the use of the X-ray mask structure,
and a method for manufacturing the X-ray mask
structure.

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Related Background Art

In recent years, there has been a tendency that
each line width of patterns on integrated circuits is
reduced as much as 70% in about three years with the
20 increase of density and processing speed of the
semiconductor integrated circuits. Owing to the
further integration of large capacity memory elements,
the further improvement of the performance of a
printing equipment is also required. Thus, it has
25 begun to demand a high performance that a transferable
minimum line width is 0.3 μm or less.

Therefore, a stepper utilizing light in an X-

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1 ray region (2 to 20 Å) as exposure wavelength light is
being developed. An X-ray mask structure for use in
such an X-ray exposing equipment has heretofore
possessed such a constitution as shown in Fig. 19F
5 formed by a manufacturing process elucidated in Figs.
19A to 19F. In this structure, nothing is formed on
the portion of an X-ray permeable film having no X-ray
absorber pattern thereon.

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10 In the concrete, reference numeral 21 is a
substrate which will be a supporting frame, and as the
substrate, an Si wafer is often used. As an X-ray
permeable film 22, there is used a thin film having a
thickness of about 2 μm and comprising silicon nitride,
silicon carbide or the like which is excellent in X-ray
15 permeability.

A chromium film having a thickness of 50 Å as a
metal thin film 23 for gold adhesion and a gold film
having a thickness of 500 Å as a plating electrode 24
for the formation of an X-ray absorber are continuously
20 deposited by EB vacuum deposition, as shown in Fig.
19A.

On the plating electrode 24, a desired fine
resist pattern 25 is formed by means of an electron
rays depicter, as shown in Fig. 19B. The resist to be
25 used may have a single-layer form or a multi-layer
form.

Next, gold is plated to form a gold film which

1 will be an X-ray absorber 26. The resist pattern 25 is
then peeled off, as shown in Fig. 19C.

The portion of the plating electrode 24 having
no X-ray absorber 26 thereon is peeled off by etching
5 with an argon gas. In this case, the plating electrode
24 and the X-ray absorber which are both made of gold
are equally etched, so that the X-ray absorber takes
such a form as represented by numeral 26' in Fig. 19D.

Afterward, the portion of the chromium thin
10 film 23 having no X-ray absorber 26' thereon is peeled
off by sputtering-etching with an argon gas or by
etching with a reactive gas (a chlorine-based gas), as
shown in Fig. 19E.

In the last place, the back of the Si wafer is
15 etched to form the supporting frame 21, as shown in
Fig. 19F.

In the conventional manufacturing process of
the X-ray mask structure, the thickness reduction of
the gold film is large and so the contrast of the X-ray
20 mask structure is poor, because a sputtering ratio of
chromium is lower as compared with that of gold, when
the portion of the chromium thin film 23 having no X-
ray absorber 26' thereon is peeled off by the
sputtering-etching with the argon gas.

25 A difficulty in the manufacture process of the
X-ray mask structure resides in that a fine pattern (on
a level of 0.25 μm) having a thickness of about 0.75 μm

1 and a high aspect ratio must be formed to obtain a
desired contrast. It makes the difficulty more
difficult to form a little thicker gold film in
consideration of a film thickness quantity which is
5 reduced at the time of the etching of chromium.
Furthermore, in the case of the etching manner using
the reactive gas, the chlorine-based gas is used, and
therefore even if the uneven state of the etching is
slight, silicon nitride or silicon carbide which is the
10 X-ray permeable film is inconveniently etched, so that
film thickness ununiformity takes place and the film
surface suffers damage. Even in the case of the
sputtering-etching manner using the argon gas, the film
thickness ununiformity occurs and the film surface
15 suffers damage.

Furthermore, when the metal thin film remains,
this remaining film has little influence on the X-ray
permeability but largely reduces alignment light
permeability. In the case that the chromium film
20 having a thickness of 50 Å remains, the X-ray
permeability deteriorates as slightly as 0.6%, but the
alignment light permeability (an He-Ne laser) lowers as
largely as 46%.

Moreover, the X-ray absorber can be formed by
25 etching W or Ta, but in this case, the reactive gases
(mainly comprising fluorine) are used. Most of these
gases have a high etching grade for silicon nitride or

1 silicon carbide constituting the X-ray permeable film,
so that the film thickness ununiformity takes place and
the film surface suffers damage. For the prevention of
these troubles, a metal thin film for an etching
5 stopper can be formed, and the film thickness
ununiformity and the damage can be inhibited as much as
the thickness of the thin film, but nevertheless the
similar problems are still present.

10 SUMMARY OF THE INVENTION

A main object of the present invention is to
provide an X-ray mask structure which can prevent
alignment light from reflecting and which has good
alignment light permeability, and a method for
15 manufacturing the X-ray mask structure.

Furthermore, another object of the present
invention is to provide an X-ray mask structure which
can solve the problems of the above-mentioned
conventional example, has an X-ray absorber pattern
20 with a sufficient contrast, even if a metal thin film
is interposed between an X-ray permeable film and a
metal capable of playing a main role as the X-ray
absorber in a manufacturing process of the X-ray mask
structure, and can inhibit most of the film thickness
25 ununiformity and the damage of the X-ray permeable film
and in which the portion of the X-ray permeable having
no pattern thereon has good alignment light

1 permeability; and a method for manufacturing the X-ray
mask structure.

Still another object of the present invention
is to provide an X-ray exposing method by which a
5 pattern can be transferred highly precisely to a
material to be exposed, and a highly precise
semiconductor device manufactured by this X-ray
exposing method.

The above-mentioned objects can be achieved by
10 the present invention. That is:

A first aspect of the present invention is
directed to an X-ray mask structure comprising an X-ray
absorber having a desired pattern, an X-ray permeable
film supporting the X-ray absorber, and a supporting
15 frame for supporting the X-ray permeable film, said X-
ray mask structure being characterized in that a metal
oxide film is formed on the portion of the X-ray
permeable film having no X-ray absorber thereon.

A second aspect of the present invention is
20 directed to an X-ray mask structure comprising an X-ray
absorber having a desired pattern, an alignment mark,
an X-ray permeable film supporting the X-ray absorber
and the mark, and a supporting frame for supporting the
X-ray permeable film, said X-ray mask structure being
25 characterized in that a metal oxide film is formed on
at least the portion of the X-ray permeable film in the
vicinity of the mark and having no X-ray absorber

1 thereon.

A third aspect of the present invention is directed to an X-ray exposing method which comprises the step of irradiating a material to be exposed with
5 X-rays through the above-mentioned X-ray mask structure.

A fourth aspect of the present invention is directed to a semiconductor device manufactured by irradiating a material to be exposed with X-rays
10 through the above-mentioned X-ray mask structure to form a circuit pattern on the material to be exposed.

A fifth aspect of the present invention is directed to a method for manufacturing an X-ray mask structure comprising an X-ray absorber having a desired
15 pattern, an X-ray permeable film supporting the X-ray absorber, and a supporting frame for supporting the X-ray permeable film, said method being characterized by having a process in which after the formation of an X-ray absorber pattern, the portion of the X-ray
20 permeable film having no X-ray absorber pattern thereon is oxidized.

A sixth aspect of the present invention is directed to a method for manufacturing an X-ray mask structure comprising an X-ray absorber having a desired
25 pattern, an X-ray permeable film supporting the X-ray absorber, and a supporting frame for supporting the X-ray permeable film, said method being characterized by

- 1 having
- (a) a process for forming a metal film on the X-ray permeable film,
- (b) a process for forming an X-ray absorber pattern on
- 5 the metal film, and
- (c) a process in which after the formation of the X-ray absorber pattern, the portion of the metal film having no X-ray absorber pattern thereon is oxidized.

10 BRIEF DESCRIPTION OF THE DRAWINGS

 Figs. 1A and 1B illustrate an example of a mask structure of the present invention.

 Fig. 2 illustrates another example of a mask structure of the present invention.

- 15 Figs. 3A to 3F illustrate a first example of an X-ray mask structure manufacturing process of the present invention.

 Fig. 4 shows partial charts of ESCA analysis of the surface of four thin film.

- 20 Figs. 5A to 5E illustrate a second example of an X-ray mask structure manufacturing process of the present invention.

- Figs. 6A to 6F illustrate a third example of an X-ray mask structure manufacturing process of the
- 25 present invention.

 Figs. 7A to 7E illustrate a fourth example of an X-ray mask structure manufacturing process of the

1 present invention.

Figs. 8A to 8F illustrate a fifth example of an x-ray mask structure process of the present invention.

5 Figs. 9A to 9E illustrate a sixth example of an X-ray mask structure manufacturing process of the present invention.

Figs. 10A to 10E illustrate a seventh example of an X-ray mask structure manufacturing process of the present invention.

10 Figs. 11A to 11E illustrate an eighth example of an X-ray mask structure manufacturing process of the present invention.

Figs. 12A to 12G illustrate a ninth example of an X-ray mask structure manufacturing process of the present invention.

Figs. 13A to 13E illustrate a tenth example of an X-ray mask structure manufacturing process of the present invention.

20 Figs. 14A to 14H illustrate an example of an X-ray mask structure manufacturing process of the present invention.

Figs. 15A to 15I illustrate a twelfth example of an X-ray mask structure manufacturing process of the present invention.

25 Figs. 16A to 16H illustrate a thirteenth example of an X-ray mask structure manufacturing process of the present invention.

1 Figs. 17A to 17E illustrate a fourteenth
example of an X-ray mask structure manufacturing
process of the present invention.

Fig. 18 is a schematic view of an X-ray
5 exposing equipment.

Figs. 19A to 19F illustrate a conventional X-
ray mask structure manufacturing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 As shown in Fig. 1A (a sectional view) and Fig.
1B (a plan view), an X-ray mask structure of the
present invention is characterized by forming a metal
oxide film 204 on the portion of an X-ray permeable
film 202 having no X-ray absorber 203 thereon.

15 In the present invention, the metal oxide film
204 mainly functions to prevent alignment light
(alignment light) from reflecting at the time of the
alignment of a material to be exposed to the X-ray mask
structure.

20 Furthermore, in the present invention, the
metal oxide film 204 is not interposed between the X-
ray permeable film 202 and the X-ray absorber 203, and
therefore adhesive properties between these films 202
and 203 are excellent, whereby the peeling off of the
25 X-ray absorber 203 can be prevented.

Here, the thickness of the metal oxide film 204
is preferably from 8 Å to 1000 Å, more preferably 20 Å

1 to 800 Å so as not to extremely lower the permeability
of the alignment light and so as to exert a further
excellent effect as the reflection preventing film. In
addition, the metal oxide film 204 can be made of an
5 oxide of a metal element having an atomic number of 35
or less, particularly an oxide of at least one metal
selected from the group consisting of chromium,
titanium, aluminum, zinc, copper and nickel.

The X-ray mask structure of the present
10 invention preferably has an intermediate layer 205 for
the further improvement of the adhesive properties
between the X-ray permeable film 202 and the X-ray
absorber 203, in addition to the metal oxide film 204,
as shown in Fig. 2 (a sectional view).

15 In the present invention, the material of the
intermediate layer 205 can be selected, considering not
only the materials of the X-ray absorber 203 and the X-
ray permeable film 202 but also mainly the material of
the metal oxide film 204. That is, the intermediate
20 layer 205 preferably comprises the metal element of the
metal oxide constituting the metal oxide film 204 in
view of the homogeneity of the films (the metal oxide
film 204 and the intermediate layer 205) formed on the
X-ray permeable film 202.

25 The X-ray absorber 203 which is one
constitutional requirement of the X-ray mask structure
of the present invention can be made of a conventional

1 known material, but preferably, it is made of a metal
having an atomic number of 70 or more which has a large
X-ray absorbency, particularly a metal such as
tantalum, tungsten, lead, gold or platinum.

5 The X-ray permeable film 202 can be made of one
or an optional combination of Be, B, C, N, Al, Si and
the like through which the X rays can permeate, but it
is preferred that the film 202 is made of SiN, SiC or
the like in view of Young's modulus, thermal expansion
10 coefficient, visible permeability and the like. No
particular restriction is put on the thickness of the
X-ray permeable film, but it is preferably in the range
of 1 to 3 μm , more preferably 1 to 2 μm .

In the X-ray mask structure of the present
15 invention, a supporting frame 201 for supporting the X-
ray permeable film 202 can be formed into an annular
shape generally from single crystal silicon. The
supporting frame may be adhered to be fixed to a
retaining frame, etc. for reinforcement. As a material
20 of retaining frame, there can be used glass materials
such as Pyrex, metal materials such as titanium,
stainless steel, etc. or ceramic materials such as
alumina, silicon carbide, etc.

In the X-ray mask structure of the present
25 invention, the metal oxide film is formed at least in
the vicinity of the alignment mark which is utilized
for the alignment between the material to be exposed

1 and the X-ray mask structure, but as shown in Figs. 1A,
1B and 2, the metal oxide film 204 can be formed all
over the surface of the X-ray permeable film 202 except
the portions covered with the X-ray absorber 203. This
5 constitution is particularly preferable, because metal
film or metal oxide film present in the X-ray absorber
patterned region can prevent the positional deviation
of the X-ray absorber due to a stress change with time
of the X-ray permeable film attributed to the oxidation
10 of the X-ray permeable film with X-ray irradiation.
That is, the metal oxide film 204 functions as a
barrier layer for preventing the oxidation with time of
the X-ray permeable film.

The X-ray mask structure of the present
15 invention preferably has the metal oxide film also on
the surface of the X-ray absorber. When the positional
precision of pattern is measured by means of light wave
interference system coordinate measuring equipment,
etc. and some displacement is found from the design
20 value for the mask pattern, the absorber pattern
surface may be subjected to oxidation treatment to
change slightly the inner stress of the absorber
pattern, thereby correcting the displacement. The
metal oxide film thus formed on the surface of the X-
25 ray absorber functions to prevent the stress change
caused by the oxidation with time of the X-ray
absorber. That is, the metal oxide film is

1 particularly preferable in that it functions as an
oxidation barrier layer of the X-ray absorber to
thereby prevent the positional deviation of the X-ray
absorber attributed to the stress change with time.

5 Also in this case, the material of the metal
oxide film is preferably an oxide of a metal element
mainly constituting the X-ray absorber in view of the
homogeneity with the X-ray absorber.

Next, reference will briefly be made to an X-
10 ray exposure method using the above-mentioned X-ray
mask structure.

Fig. 18 is a schematic view of an X-ray
exposing equipment, and reference numeral 8 is an
exposure chamber. Numeral 1 is a Be port, and 9 is an
15 exhaust port. The exposure chamber 8 is shut out from
an X-ray generation source by Be, and in the chamber,
exposure can be achieved in any state such as an
atmosphere of the air, vacuum or He. Reference numeral
2 is a mask stage, numeral 3 is an alignment detecting
portion, 4 is an X-ray mask structure, 5 is a wafer (a
20 semiconductor substrate) which is a member to be
exposed, 6 is a wafer chuck, and 7 is a wafer stage.

The X-ray mask structure 4 is mechanically set
in an approximately predetermined direction by the use
25 of an alignment pin, an orientation flat or the like,
and then adsorbed by the mask stage 2. The wafer 5 is
similarly set on the wafer chuck 6, and a relative

1 positional relation between the X-ray mask structure 4
and the wafer 5 is determined in accordance with an
indication from the alignment detecting portion 3.
Afterward,, the wafer 5 is exposed to X rays.

5 Next, reference will be made to a manufacturing
method of the X-ray mask structure of the present
invention. The method for manufacturing the X-ray mask
structure of the present invention is characterized in
that after the formation of an X-ray absorber pattern,
10 the portion of the X-ray permeable film having no X-ray
absorber pattern thereon is oxidized. Another method
for manufacturing the X-ray mask structure of the
present invention is characterized by having
(a) a process for forming a metal film on the X-ray
15 permeable film,
(b) a process for forming an X-ray absorber pattern on
the metal film, and
(c) a process in which after the formation of the X-
ray absorber pattern, the portion of the metal film
20 having no X-ray absorber pattern thereon is oxidized.

As an oxidation treatment process which is used
in the present invention, there can be preferably used
any one of an oxygen plasma treatment, an oxygen ion
injection treatment and a heat treatment in an oxygen
25 atmosphere.

Furthermore, as a metal thin film formed
between the X-ray permeable film and a metal which

1 plays the main role as the X-ray absorber on the X-ray
permeable film, any kind of metal can be used
irrespective of its application, so long as its metal
oxide in the state of the thin film obtained by the
5 above-mentioned oxidation treatment has the high
permeability of visible light or infrared rays for use
in alignment.

The thickness of the metal thin film is
preferably from 8 Å to 1000 Å, more preferably 20 Å to
10 800 Å so as to inhibit the noticeable deterioration of
the X-ray permeability, depending upon an application.
Since this kind of metal thin film has little influence
on the X-ray permeability, there is no problem, even if
it remains. Moreover, if the metal thin film is
15 oxidized, the deterioration of the alignment light
permeability can be prevented. Thus, even if the metal
thin film is not peeled off and so it remains in the X-
ray mask structure, there is not a conventional problem
that the alignment light permeability deteriorates on
20 the portion having no pattern thereon.

The material of the above-mentioned metal thin
film is preferably a metal having an atomic number of
35 or less, and the metal thin film made of such a
metal material has a low X-ray absorbency on the whole
25 and therefore it scarcely affects the X-ray
permeability. In order not to lower the alignment
light permeability, the metal thin film is oxidized

1 without peeling. When a Cr film having a thickness of
50 Å is oxidized with oxygen plasma, the permeability
deteriorates merely slightly, depending upon the
selected alignment light. In the case of an He-Ne
5 laser (6328 Å), it deteriorates as much as 1.5%, and in
the case of a semiconductor laser (8300 Å), it
deteriorates as much as 0.5% as compared with a
substrate having a thickness of 2 μm and comprising SiN
only. Thus, the metal thin film can be made of any
10 metal, so long as it is selected from the metals having
the atomic numbers of 35 or less in compliance with an
application. However, the preferable metal oxide, when
being in a thin film state, has the high permeability
of the visible light or the infrared rays used in the
15 alignment. Particularly preferable examples of the
metal for the metal thin film include chromium,
titanium, aluminum, zinc, copper or nickel. The
thickness of the metal thin film is 1,000 Å or less,
preferably 100 Å or less so as to inhibit the
20 noticeable deterioration of the X-ray permeability,
depending upon its application.

In the method for manufacturing the X-ray mask
structure of the present invention, the above-mentioned
oxidation treatment is carried out at least in the
25 vicinity of the alignment mark.

Furthermore, in the method for manufacturing
the X-ray mask structure of the present invention, an

1 oxidation treatment process of the X-ray absorber may
be contained for the purpose of providing oxidation
barrier layers for the X-ray absorber.

As the material of the X-ray absorber, there
5 can be used a metal having an atomic number of 70 or
more which possesses a large X-ray absorbency.
Preferable examples of the metal include tantalum,
tungsten, gold and platinum. These metals are scarcely
oxidized, but if treated with high energy, they can be
10 oxidized on the surfaces thereof. It has been
confirmed by an ESCA measurement that even gold which
is a noble metal can be oxidized. Prior to the
oxidation treatment, a position strain quantity of the
pattern is measured, and the oxidation is carried out
15 simultaneously with the above-mentioned oxidation
treatment to minimize the position strain quantity.

EXAMPLES

Next, the present invention will be described
20 in more detail in reference to examples shown in
drawings.

Example 1

Figs. 3A to 3F illustrate as sectional views
the first example of an X-ray mask structure
25 manufacturing process according to the present
invention.

As a material of a substrate 11 which will be a

1 supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
5 back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
of a 10% silane gas diluted with hydrogen and 20 sccm
of an ammonia gas were fed through a hole perforated in
a lower electrode. The substrate 11 was heated up to a
temperature of 250°C and a high-frequency power of 20 W
10 was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 12 of silicon nitride
having a thickness of 2 μ m.

A gold film having a thickness of 500 Å which
would be a plating electrode 14 for the formation of an
15 X-ray absorber, and a chromium film having a thickness
of 50 Å as a metal thin film 13 for adhesion were
continuously deposited by an EB vapor deposition, as
shown in Fig. 3A. A material of the metal thin film 13
is a metal capable of improving adhesive strength such
20 as Ti, Al, Sn or Zn.

An electron rays resist PMMA (trade name OEER-
1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied
thereonto, and a desired fine resist pattern 15 was
then formed by means of an electron rays depictor, as
25 shown in Fig. 3B.

Next, plating was carried out at 50°C at a
current density of 1 mA/cm² by the use of a gold sulfite

1 plating solution (trade name Neutronex 309, made by
EEJA) to form a gold film which would be an X-ray
absorber 16. Afterward, the resist pattern 15 was
peeled off with an exclusive peeling solution, as shown
5 in Fig. 3C.

The portion of the plating electrode 14 having
no X-ray absorber 16 thereon was peeled off by means of
an RIE equipment.

Back pressure was reduced to 1×10^{-5} Torr, and
10 20 sccm of an argon gas was fed and 200 W was then
applied under 5×10^{-2} Torr to carry out etching. Since
the plating electrode 14 and the X-ray absorber were
both made of gold, they were equally etched, so that
the X-ray absorber took a conformation denoted by 16'
15 in Fig. 3D.

Furthermore, 20 sccm of an oxygen gas was fed
to the same RIE equipment and 130 W was then applied
under 5×10^{-2} Torr, so that the portion of the metal
thin film 13 having no pattern thereon was converted
20 into chromium oxide 17 with oxygen plasma, as shown in
Fig. 3E.

In the last place, the back of the Si wafer was
etched at 110°C with a 30% by weight aqueous potassium
hydroxide solution to form a supporting frame 11, as
25 shown in Fig. 3F.

In order to confirm that the film obtained by

1 oxidizing the metal thin film 13 in Fig. 3E in such a
manufacturing process was chromium oxide, the surface
of the oxidized film was analyzed by ESCA. For the
following four kinds of films in addition to a sample
5 for comparison, the analysis was carried out. Fig. 4
shows partial charts containing peaks of Cr.

(1) The film 17 in Fig. 3E obtained by
oxidizing the metal thin film 13.

(2) The metal thin film 13 in Fig. 3D (after
10 the portion of the plating electrode 14 having no
pattern thereon was peeled off).

(3) The untreated silicon nitride film 12.

(4) The silicon nitride film in Fig. 3E after
the metal thin film 13 was peeled off.

15 From the observation of Fig. 4, it is apparent
that Cr was not present in the film (3). In the film
(4), there was a small peak at the same position as in
the film (2), and therefore it seemed that Cr remained.
In fact, the measurement was made after the film was
20 exposed to air, and thus Cr on the outermost surface
was slightly oxidized. In the case of the film (1), a
peak shifted toward the side of higher energy, which
indicated that chromium was further oxidized, as
compared with these two films (3) and (4). The films
25 (1) and (4) had about the same values of light
permeability, but according to the values measured by
ESCA, the film (4) only had the same Si peak as in the

1 film (3). Thus, it was confirmed from the foregoing
that in the film (1), chromium oxide was still present
in contrast to the film (4) from which the metal thin
film 13 was peeled off.

5 As described above, chromium of the thin film
for adhesion was oxidized without etching, and thus,
there could be prevented the thickness decrease of the
gold thin film which was the X-ray absorber 16' and the
generation of the film thickness ununiformity of
10 silicon nitride constituting the X-ray permeable film.
Furthermore, owing to the presence of chromium oxide 17
in the portion having no pattern thereon, the
deterioration of the permeability was inhibited. That
is, in the case of X rays, the deterioration of the
15 permeability was only 0.6% and in the case of an He-Ne
laser (6328 Å) for use in alignment, that of the
permeability was 1.5%, and so there was no problem.

Example 2

20 Figs. 5A to 5E illustrate as sectional views
the second example of an X-ray mask structure
manufacturing process according to the present
invention.

As a material of a substrate 31 which will be a
supporting frame, an Si wafer is often used, and in
25 this example, an Si wafer having a diameter of 3 inches
and a thickness of 1 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,

1 back pressure was reduced to 1×10^{-6} Torr, and 10 sccm
of a 10% silane gas diluted with hydrogen and 10 sccm
of a methane gas were fed through a hole perforated in
a lower electrode. The substrate 31 was heated up to a
5 temperature of 650°C and a high-frequency power of 50 W
was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 32 of silicon carbide
having a thickness of 2 μm .

Afterward, the film was set on a two-
10 dimensional sputtering equipment, and after back
pressure was reduced to 2×10^{-6} Torr, 10 sccm of an
argon gas was fed thereto and a high frequency power of
100 W was then applied at a substrate temperature of
150 $^{\circ}\text{C}$ under a pressure of 10×10^{-2} Torr to form a
15 chromium film having a thickness of 200 $\text{\AA}$ which would
be a metal thin film 33 for an absorber etching
stopper. Furthermore, 500 W was continuously applied,
thereby forming a W film of 8000 $\text{\AA}$ in thickness which
would be an X-ray absorber 36, as shown in Fig. 5A.

20 As a material of the metal thin film, any metal
can be used, so long as it is such as to have some
difference of an etching grade as compared with a metal
for the X-ray absorber.

The back of the Si wafer was etched at 110°C
25 with a 30% by weight aqueous potassium hydroxide
solution to form a supporting frame 31, as shown in
Fig. 5B.

1 PIQ (trade name, made by Hitachi Chemical Co.,
Ltd.) which would be a lower resist layer and SNR
(trade name, made by Toyo Soda Mfg. Co., Ltd.) which
would be an upper resist layer containing Si were
5 applied thereonto, and a desired fine resist pattern 35
was then formed by an electron rays depositor and an RIE
equipment, as shown in Fig. 5C.

Next, W which would be an X-ray absorber 36 was
etched by means of an RIE equipment. After back
10 pressure was reduced to 1×10^{-5} Torr, 50 sccm of a CF_4
gas was fed and 200 W was then applied under 5×10^{-2}
Torr to etch W. Since scarcely etched with the CF_4 gas,
chromium was not damaged, so that the X-ray absorber
took a conformation represented by 36', as shown in
15 Fig. 5D. The resist pattern 35 was etched
simultaneously with the etching of W, but its remaining
portion was peeled off with an exclusive peeling
solution.

Afterward, in an ion injector, oxygen ions were
20 injected at an oxygen ion concentration of 10^{16} - 10^{17}
ions/cm² at 10-20 KV to convert the portion of the metal
thin film 33 having no pattern thereon into chromium
oxide 37, as shown in Fig. 5E. When the ion injection
is used at the suitably selected ion concentration and
25 accelerating voltage, even the relatively thick film
can be oxidized. Therefore, the metal thin film may be
formed so that chromium oxide may have such a thickness

1 as to become a reflection preventing film (630 Å in the
case of an He-Ne laser).

As described above, the metal thin film of
chromium which was an etching stopper was oxidized
5 without peeling, and thus, there could be prevented the
generation of the film thickness ununiformity of
silicon carbide constituting the X-ray permeable film.
Furthermore, owing to the presence of chromium oxide 37
in the portion having no pattern thereon, the
10 deterioration of the permeability was inhibited. That
is, in the case of X rays, the deterioration of the
permeability was only 2.3% and in the case of an He-Ne
laser (6328 Å) for use in alignment, that of the
permeability was 5.0%, and so there was no problem.

15 Example 3

Figs. 6A to 6F illustrate as sectional views
the third example of an X-ray mask structure
manufacturing process according to the present
invention.

20 As a material of a substrate 41 which will be a
supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
25 back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
of a 10% silane gas diluted with hydrogen and 20 sccm
of an ammonia gas were fed through a hole perforated in

1 a lower electrode. The substrate 41 was heated up to a
temperature of 250°C and a high-frequency power of 20 W
was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 42 of silicon nitride
5 having a thickness of 2 μm .

Next, the back of the Si wafer was etched at
110°C with a 30% by weight aqueous potassium hydroxide
solution to form a supporting frame 41, as shown in
Fig. 6A.

10 A gold film having a thickness of 500 Å which
would be a plating electrode 44 for the formation of an
X-ray absorber, and a titanium film having a thickness
of 50 Å as a metal thin film 43 for adhesion were
continuously deposited by an EB vapor deposition, as
15 shown in Fig. 6B.

An electron rays resist PMMA (trade name OEER-
1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied
thereonto, and a desired fine resist pattern 45 was
then formed by means of an electron rays depictor, as
20 shown in Fig. 6C.

Next, plating was carried out at 50°C at a
current density of 0.5 mA/cm² by the use of a gold
sulfite plating solution (trade name Neutronex 309,
made by EEJA) to form a gold film which would be an X-
25 ray absorber 46. Afterward, the resist pattern 45 was
peeled off with an exclusive peeling solution, as shown
in Fig. 6D.

1 The portion of the plating electrode 44 having
no X-ray absorber 46 thereon was peeled off by means of
an RIE equipment.

 Back pressure was reduced to 1×10^{-5} Torr, and
5 20 sccm of an argon gas was fed and 200 W was then
applied under 5×10^{-2} Torr to carry out etching. Since
the plating electrode 44 and the X-ray absorber were
both made of gold, they were equally etched, so that
the X-ray absorber took a conformation denoted by 46'
10 in Fig. 6E.

 Next, a heat treatment was carried out at 100°C
in an oxygen atmosphere to convert the portion of the
metal thin film 43 having no pattern thereon into
titanium oxide 47, as shown in Fig. 6F.

15 As described above, titanium of the metal thin
film for adhesion was oxidized without peeling, and
thus, there could be prevented the thickness reduction
of the gold film which was the X-ray absorber 46' and
the generation of the film thickness ununiformity of
20 silicon nitride constituting the X-ray permeable film.
Furthermore, owing to the presence of titanium oxide 47
in the portion having no pattern thereon, the
deterioration of permeability was inhibited. That is,
in the case of X rays, the deterioration of the
25 permeability was only 0.3% and in the case of an He-Ne
laser (6328 Å) for use in alignment, that of the
permeability was 1.0%, and so there was no problem.

1 Example 4

 Figs. 7A to 7E illustrate as sectional views
the fourth example of an X-ray mask structure
manufacturing process according to the present
5 invention.

 As a material of a substrate 61 which would be
a supporting frame, an Si wafer was used. A silicon
nitride film having a thickness of 2 μm was formed in
the same manner as in Example 3 to obtain an X-ray
10 permeable film 62.

 A nickel film having a thickness of 200 Å as a
metal thin film 63 which would be a plating electrode
for the formation of an X-ray absorber was deposited by
an EB deposition, as shown in Fig. 7A.

15 An electron rays resist PMMA (trade name OEER-
1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied
thereonto, and a desired fine resist pattern 65 was
then formed by means of an electron rays depictor, as
shown in Fig. 7B.

20 Next, plating was carried out at 50°C at a
current density of 0.5 mA/cm² by the use of a gold
sulfite plating solution (trade name Neutronex 309,
made by EEJA) to form a gold film which would be an X-
ray absorber 66. Afterward, the resist pattern 65 was
25 peeled off with an exclusive peeling solution, as shown
in Fig. 7C.

 Afterward, in an ion injector, oxygen ions were

1 injected at an oxygen ion concentration of 10^{16} - 10^{17}
ions/cm² at 10-20 KV to convert the portion of the metal
thin film 63 having no pattern thereon into nickel
oxide 67, as shown in Fig. 7D.

5 As described above, the nickel film which was
the metal thin film for adhesion was oxidized without
peeling, and thus, there could be prevented the
thickness reduction of the gold film which was the X-
ray absorber 66' and the generation of the film
10 thickness ununiformity of silicon nitride constituting
the X-ray permeable film. Furthermore, owing to the
presence of titanium oxide 67 in the portion having no
pattern thereon, the deterioration of permeability was
inhibited. That is, in the case of X rays, the
15 deterioration of the permeability was only 4.2% and in
the case of an He-Ne laser (6328 Å) for use in
alignment, that of the permeability was 5.0%, and so
there was no problem.

In addition, when exposed to the X rays, the
20 thickness reduction of the X-ray absorber was slight,
so that a sufficient contrast could be obtained, and
thus a high precise semiconductor chip could be
prepared.

Example 5

25 Figs. 8A to 8F illustrate as sectional views
the fifth example of an X-ray mask structure
manufacturing process according to the present

1 invention.

As a material of a substrate 51 which will be a supporting frame, an Si wafer is often used, and in this example, an Si wafer having a diameter of 3 inches
5 and a thickness of 2 mm was used. This substrate was set on a plasma CVD equipment.

In the first place, back pressure was reduced to 2×10^{-6} Torr, and 5 sccm of a 10% silane gas diluted with hydrogen and 20 sccm of an ammonia gas were fed
10 through a hole perforated in a lower electrode. The substrate 51 was heated up to a temperature of 250°C and a high-frequency power of 20 W was then applied under a pressure of 5×10^{-3} Torr to form an X-ray permeable film 52 of silicon nitride having a thickness
15 of 2 μm .

A gold film having a thickness of 500 Å which would be a plating electrode 54 for the formation of an X-ray absorber, and a chromium film having a thickness of 50 Å as a metal thin film 53 for adhesion were
20 continuously deposited by an EB vapor deposition, as shown in Fig. 8A. A material of the metal thin film 53 is a metal capable of improving adhesive strength such as Ti, Al or Zn.

An electron rays resist PMMA (trade name OE8R-
25 1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied thereonto, and a desired fine resist pattern 55 was then formed by means of an electron rays depictor, as

1 shown in Fig. 8B.

Next, plating was carried out at 50°C at a
current density of 1 mA/cm² by the use of a gold sulfite
plating solution (trade name Neutronex 309, made by
5 EEJA) to form a gold film which would be an X-ray
absorber 56. Afterward, the resist pattern 55 was
peeled off with an exclusive peeling solution, as shown
in Fig. 8C. The portion of the plating electrode 54
having no X-ray absorber 56 thereon was peeled off by
10 means of an RIE equipment. Back pressure was reduced
to 1×10^{-5} Torr, and 20 sccm of an argon gas was fed
and 200 W was then applied under 5×10^{-2} Torr to carry
out etching. Since the plating electrode 54 and the X-
ray absorber were both made of gold, they were equally
15 etched, so that the X-ray absorber took a conformation
denoted by 56' in Fig. 8D.

Furthermore, the back of the Si wafer was
etched at 110° with a 30% by weight potassium hydroxide
to form a supporting frame 51, as shown in Fig. 8E. At
20 this time, a pattern position strain quantity of the X-
ray absorber 56' was measured by means of a light wave
interference system coordinate measuring equipment, and
it was 0.3 μm. Oxidizing conditions were selected
taking this strain quantity into consideration.

25 In the last place, 20 sccm of an oxygen gas was
fed to the same RIE equipment, and 200 W was then
applied under 5×10^{-2} Torr, so that by oxygen plasma,

1 the surface portion of the X-ray absorber 56' was
converted into gold oxide 57 and the portion of the
metal thin film 53 having no pattern thereon was
converted into chromium oxide 58, as shown in Fig. 8F.
5 It is difficult to oxidize gold; but when large energy
is applied, the uppermost surface can be only oxidized.

As understood from the above, when chromium of
the thin film for adhesion was oxidized without
etching, there could be prevented the thickness
10 decrease of the gold thin film which was the X-ray
absorber 56' and the generation of the film thickness
ununiformity of silicon nitride constituting the X-ray
permeable film. Furthermore, owing to the presence of
chromium oxide 58 in the portion having no pattern
15 thereon, the deterioration of permeability was
inhibited. That is, in the case of X rays, the
deterioration of the permeability was only 0.6% and in
the case of an He-Ne laser (6328 Å) for use in
alignment, that of the permeability was 1.5%, and so
20 there was no problem. In addition, when the position
strain quantity of the X-ray absorber 56' was measured
again by means of the light wave interference system
coordinate measuring equipment, it decreased to 0.03 μm
(the limit of measurement). Thus, the product can be
25 used as a highly precise X-ray mask structure.

Example 6

Figs. 9A to 9E illustrate as sectional views

1 the sixth example of an X-ray mask structure
manufacturing process according to the present
invention.

As, a material of a substrate 71 which will be a
5 supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 1 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
back pressure was reduced to 1×10^{-6} Torr, and 10 sccm
10 of a 10% silane gas diluted with hydrogen and 10 sccm
of a methane gas were fed through a hole perforated in
a lower electrode. The substrate 71 was heated up to a
temperature of 650°C and a high-frequency power of 50 W
was then applied under a pressure of 5×10^{-3} Torr to
15 form an X-ray permeable film 72 of silicon carbide
having a thickness of 2 μ m.

Afterward, the film was set on a two-
dimensional sputtering equipment, and after back
pressure was reduced to 2×10^{-6} Torr, 10 sccm of an
20 argon gas was fed thereto and a high frequency power of
100 W was then applied at a substrate temperature of
150°C under a pressure of 10×10^{-2} Torr to form a
chromium film having a thickness of 200 Å which would
be a metal thin film 73 for an absorber etching
25 stopper. Furthermore, 500 W was continuously applied,
thereby forming a W film of 8000 Å in thickness which
would be an X-ray absorber 76, as shown in Fig. 9A. As

1 a material of the metal thin film 73, any metal can be
used, so long as it is such as to have some difference
of an etching grade as compared with a metal for the
X-ray absorber.

5 The back of the Si wafer was etched at 110°C
with a 30% by weight aqueous potassium hydroxide
solution to form a supporting frame 21, as shown in
Fig. 9B. PIQ (trade name, made by Hitachi Chemical
Co., Ltd.) which would be a lower resist layer and SNR
10 (trade name, made by Toyo Soda Mfg. Co., Ltd.) which
would be an upper resist layer containing Si were
applied thereonto, and a desired fine resist pattern 75
was then formed by an electron rays depictor, as shown
in Fig. 9C.

15 Next, W which would be an X-ray absorber 76 was
etched by means of an RIE equipment. After back
pressure was reduced to 1×10^{-5} Torr, 50 sccm of a CF_4
gas was fed and 200 W was then applied under 5×10^{-2}
Torr to etch W.

20 Since scarcely etched with the CF_4 gas, chromium
was not damaged, so that the X-ray absorber took a
conformation represented by 76', as shown in Fig. 9D.
The resist pattern 75 was etched simultaneously with
the etching of W, but its remaining portion was peeled
25 off with an exclusive peeling solution. At this time,
a pattern position strain quantity of the X-ray
absorber 76' was measured by means of a light wave

1 interference system coordinate measuring equipment, and
it was 0.5 μm . Oxidizing conditions were selected
taking this strain quantity into consideration.

20, sccm of an oxygen gas was fed to the same
5 RIE equipment, and 130 W was then applied under 5×10^{-2}
Torr, so that by oxygen plasma, the surface portion of
the X-ray absorber 76' was converted into tungsten
oxide 77 and the portion of the metal thin film 73
having no pattern thereon was converted into chromium
10 oxide 78, as shown in Fig. 9E.

As described above, the metal thin film of
chromium which was an etching stopper was oxidized
without peeling, there could be prevented the
generation of the film thickness ununiformity of
15 silicon nitride constituting the X-ray permeable film.
Furthermore, owing to the presence of chromium oxide 77
in the portion having no pattern thereon, the
deterioration of permeability was inhibited. That is,
in the case of X rays, the deterioration of the
20 permeability was only 2.3% and in the case of an He-Ne
laser (6328 $\text{\AA}$) for use in alignment, that of the
permeability was 5.0%, and so there was no problem. In
addition, when the position strain quantity of the X-
ray absorber 76' was measured again by means of the
25 light wave interference system coordinate measuring
equipment, it decreased to 0.05 μm . Thus, the product
can be used as a highly precise X-ray mask structure.

1 Example 7

 Figs. 10A to 10E illustrate as sectional views
the seventh example of an X-ray mask structure
manufacturing process according to the present
5 invention.

 As a material of a substrate 81 which will be a
supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
10 set on a plasma CVD equipment. In the first place,
back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
of a 10% silane gas diluted with hydrogen and 20 sccm
of an ammonia gas were fed through a hole perforated in
a lower electrode. The substrate 81 was heated up to a
15 temperature of 250°C and a high-frequency power of 20 W
was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 82 of silicon nitride
having a thickness of 2 μ m. Next, the back of the Si
wafer was etched at 110°C with a 30% by weight aqueous
20 potassium hydroxide solution to form a supporting frame
81, as shown in Fig. 10A.

 Afterward, the film was set on a two-
dimensional sputtering equipment, and after back
pressure was reduced to 2×10^{-6} Torr, 10 sccm of an
25 argon gas was fed thereto and a high frequency power of
100 W was then applied at a substrate temperature of
150°C under a pressure of 10×10^{-2} Torr to form a

1 chromium film having a thickness of 100 Å which would
be a metal thin film 83 for an absorber etching
stopper. Furthermore, 500 W was continuously applied,
thereby forming a W film of 8000 Å in thickness which
5 would be an X-ray absorber 86, as shown in Fig. 10B.
As a material of the metal thin film 83, any metal can
be used, so long as it is such as to have some
difference of an etching grade as compared with a metal
for the X-ray absorber.

10 An electron rays resist PMMA (trade name OEER-
1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied
thereonto, and a desired fine resist pattern 85 was
then formed by means of an electron rays depictor, as
shown in Fig. 10C.

15 Next, W which would be the X-ray absorber 86
was etched by means of an RIE equipment. After back
pressure was reduced to 1×10^{-5} Torr, 50 sccm of a CF_4
gas was fed and 200 W was then applied under 5×10^{-2}
Torr to etch W. Since scarcely etched with the CF_4 gas,
20 chromium was not damaged, so that the X ray-absorber
took a conformation represented by 86', as shown in
Fig. 10D. The resist pattern 85 was etched
simultaneously with the etching of W, but its remaining
portion was peeled off with an exclusive peeling
25 solution.

At this time, a pattern position strain
quantity of the X-ray absorber 86' was measured by

1 means of a light wave interference system coordinate
measuring equipment, and it was 0.3 μm . Oxidizing
conditions were selected taking this strain quantity
into consideration. Next, a heat treatment was carried
5 out at 100°C in an oxygen atmosphere, whereby the
outermost surface of the absorber 86' was converted
into tungsten oxide 87 and the portion of the metal
thin film 83 having no pattern thereon was converted
into chromium oxide 88, as shown in Fig. 10E. As
10 understood from the above, chromium constituting the
thin film for adhesion was oxidized without peeling,
and thus, there could be prevented the thickness
reduction of gold constituting the X-ray absorber 86'
and the generation of the film thickness ununiformity
15 of silicon nitride constituting the X-ray permeable
film.

Furthermore, owing to the presence of chromium
oxide 88 in the portion having no pattern thereon, the
deterioration of permeability was inhibited. That is,
20 in the case of X rays, the deterioration of the
permeability was only 0.3% and in the case of an He-Ne
laser (6328 Å) for use in alignment, that of the
permeability was 1.0%, and so there was no problem. In
addition, when the position strain quantity of the X-
25 ray absorber 86' was measured again by means of the
light wave interference system coordinate measuring
equipment, it decreased to 0.05 μm . Thus, the product

1 can be used as a highly precise X-ray mask structure.

Example 8

Figs. 11A to 11E illustrate as sectional views
the eighth example of an X-ray mask structure
5 manufacturing process according to the present
invention.

As a material of a substrate 91 which would be
a supporting frame, an Si wafer was used, and a silicon
nitride film having a thickness of 2 μm was formed as
10 an X-ray permeable film 92 in the same manner as in
Example 7.

A nickel film having a thickness of 200 Å as a
metal thin film 93 which would be a plating electrode
for the formation of an X-ray absorber was deposited by
15 an EB vapor deposition, as shown in Fig. 11A. An
electron rays resist PMMA (trade name OEER-1000, made
by Tokyo Oka Kogyo Co., Ltd.) was applied thereonto,
and a desired fine resist pattern 95 was then formed by
means of an electron rays depictor, as shown in Fig.
20 11B.

Next, plating was carried out at 50°C at a
current density of 0.5 mA/cm² by the use of a gold
sulfite plating solution (trade name Neutronex 309,
made by EEJA) to form a gold film which would be an X-
25 ray absorber 96. Afterward, the resist pattern 95 was
peeled off with an exclusive peeling solution, as shown
in Fig. 11C. Afterward, the back of the Si wafer was

1 etched at 110°C with a 30% by weight aqueous potassium
hydroxide solution to form a supporting frame 91, as
shown in Fig. 11D. At this time, a pattern position
strain quantity of the X-ray absorber 96 was measured
5 by means of a light wave interference system coordinate
measuring equipment, and the measured maximum strain
quantity was 0.2 μm . Oxidizing conditions were
selected taking this strain quantity into
consideration.

10 In the last place, in an ion injector, oxygen
ions were injected at an oxygen ion concentration of
 10^{16} - 10^{17} ions/cm² at 20-30 KV, whereby the outermost
surface of the absorber 96 was converted into gold
oxide 97 and the portion of the metal thin film 93
15 having no pattern thereon was converted into nickel
oxide 98, as shown in Fig. 11D. When the ion injection
is used at the suitably selected ion concentration and
accelerating voltage, even the relatively thick film
can be oxidized. Therefore, the metal thin film may be
20 formed so that nickel oxide may have such a thickness
as to become a reflection preventing film (690 Å in the
case of an He-Ne laser).

As described above, nickel of the thin film was
oxidized without peeling, and thus, there could be
25 prevented the thickness reduction of gold constituting
the X-ray absorber 96 and the generation of the film
thickness ununiformity of silicon nitride constituting

1 the X-ray permeable film. Furthermore, owing to the
presence of nickel oxide 97 in the portion having no
pattern thereon, the deterioration of permeability was
inhibited. That is, in the case of X rays, the
5 deterioration of the permeability was only 4.2% and in
the case of an He-Ne laser (6328 Å) for use in
alignment, that of the permeability was 5.0%, and so
there was no problem. In addition, when the position
strain quantity of the X-ray absorber 96 was measured
10 again by means of the light wave interference system
coordinate measuring equipment, it decreased to 0.03 μm
(the limit of measurement). Thus, the product can be
used as a highly precise X-ray mask structure.

Example 9

15 Figs. 12A to 12G illustrate as sectional views
the ninth example of an X-ray mask structure
manufacturing process according to the present
invention.

As a material of a substrate 101 which will be
20 a supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 1 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
back pressure was reduced to 1×10^{-6} Torr, and 10 sccm
25 of a 10% silane gas diluted with hydrogen and 10 sccm
of a methane gas were fed through a hole perforated in
a lower electrode. The substrate 101 was heated up to

1 a temperature of 650°C and a high-frequency power of 50
W was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 102 of silicon carbide
having a thickness of 2 μm .

5 Afterward, the film was set on a two-
dimensional sputtering equipment, and after back
pressure was reduced to 2×10^{-6} Torr, 10 sccm of an
argon gas was fed thereto and a high frequency power of
100 W was then applied at a substrate temperature of
10 150°C under a pressure of 10×10^{-2} Torr to form a
chromium film having a thickness of 50 nm which would
be a metal thin film 103 for an absorber etching
stopper. Furthermore, 500 W was continuously applied,
thereby forming a W film of 800 nm in thickness which
15 would be an X-ray absorber 106, as shown in Fig. 12A.
As a material of the metal thin film 103, any metal can
be used, so long as it is such as to have some
difference of an etching grade as compared with a metal
for the X-ray absorber. The back of the Si wafer was
20 etched at 110°C with a 30% by weight aqueous potassium
hydroxide solution to form a supporting frame 101, as
shown in Fig. 12B.

PIQ (trade name, made by Hitachi Chemical Co.,
Ltd.) which would be a lower resist layer and SNR
25 (trade name, made by Toyo Soda Mfg. Co., Ltd.) which
would be an upper resist layer containing Si were
applied thereonto, and a desired fine resist pattern

1 105 was then formed by an electron rays depositor, as
shown in Fig. 12C.

Next, W which would be an X-ray absorber 106
was etched by means of an RIE equipment. After back
5 pressure was reduced to 1×10^{-5} Torr, 50 sccm of a CF_4
gas was fed and 200 W was then applied under 5×10^{-2}
Torr to etch W. Since scarcely etched with the CF_4 gas,
chromium was not damaged, so that the X-ray absorber
took conformations represented by 106' and an alignment
10 mark 107, as shown in Fig. 12D. The resist pattern 105
was etched simultaneously with the etching of W, but
its remaining portion was peeled off with an exclusive
peeling solution. A protective film 109 was formed
with a novolak resist (trade name AZ-1370SF, made by
15 Tokyo Oka Kogyo Co., Ltd.) on a circuit pattern
portion, as shown in Fig. 12E.

Afterward, 20 sccm of an oxygen gas was fed to
the RIE equipment, and 200 W was then applied under $5 \times$
 10^{-2} Torr, so that by the irradiation of oxygen plasma,
20 the portion of the metal thin film 103 having no
alignment mark thereon which would be used for
alignment was converted into a chromium oxide film
having a thickness of 63 nm which would be a reflection
preventing film 108, as shown in Fig. 12F. The
25 remaining portion of the protective film 109 was peeled
off with an exclusive peeling solution, as shown in
Fig. 12G.

1 As described above, the portion of the metal
thin film of chromium as an etching stopper on which
any alignment mark was not formed and which would be
used for the alignment was oxidized without peeling to
5 form the reflection preventing film, whereby there
could be prevented the reflection of alignment light,
the generation of the positional deviation of tungsten
constituting the X-ray absorber 106' due to the stress
or its change of chromium oxide, the thickness
10 reduction of the tungsten film, the generation of film
thickness ununiformity in the range of silicon carbide
constituting the X-ray permeable film usable for the
alignment, and the damage of the film surface.

 This X-ray mask structure was set on an
15 exposure chamber 8 (Fig. 18), and alignment was then
carried out by the use of the alignment light from an
He-Ne laser (633 nm). As a result, a stable alignment
light permeability could be obtained, and the precise
alignment could be attained. In addition, when exposed
20 to the X rays, the thickness reduction of the X-ray
absorber was slight, so that a sufficient contrast
could be obtained and the generation of the positional
deviation could be prevented, and thus a highly precise
semiconductor chip could be prepared.

25 Example 10

 Figs. 13A to 13E illustrate as sectional views
the tenth example of an X-ray mask structure

1 manufacturing process according to the present
invention.

As a material of a substrate 111 which will be
a supporting frame, an Si wafer is often used, and in
5 this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
of a 10% silane gas diluted with hydrogen and 20 sccm
10 of an ammonia gas were fed through a hole perforated in
a lower electrode. The substrate 111 was heated up to
a temperature of 350°C and a high-frequency power of 20
W was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 112 of silicon nitride
15 having a thickness of 2 μ m.

A nickel film having a thickness of 55 nm as a
metal thin film 113 which would be a plating electrode
for the formation of an X-ray absorber was deposited by
an EB vapor deposition, as shown in Fig. 13A. The back
20 of the Si wafer was then etched at 110°C with a 30% by
weight aqueous potassium hydroxide solution to form a
supporting frame 111, as shown in Fig. 13B. An
electron rays resist PMMA (trade name OEER-1000, made
by Tokyo Oka Kogyo Co., Ltd.) was applied thereonto,
25 and a desired fine resist pattern 115 was then formed
by means of an electron rays depictor, as shown in Fig.
13C.

1 Next, plating was carried out at 50°C at a
current density of 0.5 mA/cm² by the use of a gold
sulfite plating solution (trade name Neutronex 309,
made by EEJA) to form a gold film which would be an X-
5 ray absorber 116 and an alignment mark 117. Afterward,
the resist pattern 115 was peeled off with an exclusive
peeling solution, as shown in Fig. 13D.

 In the last place, in a focusing ion injector,
oxygen ions were injected at an oxygen ion
10 concentration of 10¹⁶-10¹⁷ ions/cm² at 60-70 KV, whereby
the region of the metal thin film 113 on which the
alignment mark was not formed and which would be used
for the alignment was oxidized to form a nickel oxide
film having a thickness of 69 nm as a reflection
15 preventing film 118, as shown in Fig. 13E.

 As described above, the region of the metal
thin film on which the alignment mark was not formed
and which would be used for the alignment was only
oxidized without peeling to form the reflection
20 preventing film, whereby there could be prevented the
reflection of alignment light, the positional deviation
of the X-ray absorber 116 of gold due to the stress or
its change of nickel oxide, the thickness reduction of
the gold film, the generation of film thickness
25 ununiformity in the region of silicon nitride
constituting the X-ray permeable film which would be
used for the alignment, and the damage of the film

1 surface.

This X-ray mask structure was set on an exposure chamber 8 (Fig. 18), and alignment was then carried out by the use of the alignment light from an He-Ne laser (633 nm). As a result, a stable alignment light permeability could be obtained, and the precise alignment could be attained. In addition, when exposed to the X rays, the thickness of the X-ray absorber was not decreased, so that a sufficient contrast could be obtained, and the positional deviation could also be prevented. In consequence, a highly precise semiconductor chip could be prepared.

Example 11

Figs. 14A to 14H illustrate as sectional views the eleventh example of an X-ray mask structure manufacturing process according to the present invention.

As a material of a substrate 121 which will be a supporting frame, an Si wafer is often used, and in this example, an Si wafer having a diameter of 3 inches and a thickness of 2 mm was used. This substrate was set on a plasma CVD equipment.

In the first place, back pressure was reduced to 2×10^{-6} Torr, and 5 sccm of a 10% silane gas diluted with hydrogen and 20 sccm of an ammonia gas were fed through a hole perforated in a lower electrode. The substrate 121 was heated up to a temperature of 250°C

1 and a high-frequency power of 20 W was then applied
under a pressure of 5×10^{-3} Torr to form an X-ray
permeable film 122 of silicon nitride having a
thickness of 2 μm .

5 Afterward, this substrate was set on a
sputtering equipment, and a chromium oxide film 128
having a thickness of 57 nm and constituting a part of
a reflection preventing film was formed, as shown in
Fig. 14A. The resist was patterned into a shape of a
10 scribe line corresponding to the peripheral portion of
a circuit pattern, and then etched to form a part 128'
of the reflection preventing film having the scribe
line shape. The remaining resist, if any, was peeled
off, as shown in Fig. 14B.

15 A gold film having a thickness of 50 nm which
would be a plating electrode 124 for the formation of
an X-ray absorber and a chromium film having a
thickness of 5 nm as a metal thin film 123 for adhesion
were continuously deposited by an EB vapor deposition,
20 as shown in Fig. 14C.

 An electron rays resist PMMA (trade name OEER-
1000, made by Tokyo Oka Kogyo Co., Ltd.) was applied
thereonto, and a desired fine resist pattern 125 was
then formed by means of an electron rays depictor, as
25 shown in Fig. 14D. Next, plating was carried out at
50°C at a current density of 1 mA/cm² by the use of a
gold sulfite plating solution (trade name Neutronex

1 309, made by EEJA) to form a gold film which would be
an X-ray absorber 126 and an alignment mark 127.

Afterward, the resist pattern 125 was peeled off with
an exclusive peeling solution, as shown in Fig. 14E.

5 The portion of the plating electrode 124 on
which the X-ray absorber 126 and the alignment mark 127
were not formed was peeled off by means of an RIE
equipment. After back pressure was reduced to 1×10^{-5}
Torr, 20 sccm of an argon gas was fed thereto and 200 W
10 was then applied under a pressure of 5×10^{-2} Torr to
carry out etching. Since the plating electrode 124,
the X-ray absorber 126 and the alignment mark 127 were
all made of gold, they were equally etched, so that the
X-ray absorber and the alignment mark took the
15 conformations of 126' and 127', as shown in Fig. 14F.

Afterward, 20 sccm of an oxygen gas was fed to
the RIE equipment, and 200 W was then applied thereonto
under 5×10^{-2} Torr and thus the laminate was irradiated
with oxygen plasma, whereby the portion of the metal
20 thin film 123 having no pattern thereon was converted
into chromium oxide, with the result that a chromium
oxide film having a thickness of 63 nm was formed as a
reflection preventing film 128" in addition to the
previously formed film 128', as shown in Fig. 14G.

25 In the last place, the back of the Si wafer was
etched at 110°C with a 30% by weight aqueous potassium
hydroxide solution to form a supporting frame 121, as

1 shown in Fig. 14H.

As shown in Fig. 14H, the chromium oxide film was formed all over the portion of the X-ray permeable film having no pattern thereon. However, since the
5 chromium oxide film was as thin as 7 nm, the positional deviation of the X-ray absorber 126' was not brought about by the stress or its change of the film. The portion of the metal thin film 123 on the scribe line having no alignment mark thereon functioned as the
10 reflection preventing film together with the previously formed chromium oxide. Furthermore, the thickness reduction of the gold film which was the X-ray absorber 126' could be prevented.

This X-ray mask structure was set on an
15 exposure chamber 8 (Fig. 18), and alignment was then carried out by the use of alignment light from an He-Ne laser (633 nm). As a result, a stable alignment light permeability could be obtained, and the highly precise alignment could be attained. In addition, when exposed
20 to the X rays, the thickness of the X-ray absorber was not decreased, so that a sufficient contrast could be obtained, and the positional deviation could also be prevented. In consequence, a highly precise semiconductor chip could be prepared.

25 Example 12

Figs. 15A to 15H illustrate as sectional views the twelfth example of an X-ray mask structure

1 manufacturing process according to the present
invention.

As a material of a substrate 131 which will be
a supporting frame, an Si wafer is often used, and in
5 this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
of a 10% silane gas diluted with hydrogen and 20 sccm
10 of an ammonia gas were fed through a hole perforated in
a lower electrode. The substrate 131 was heated up to
a temperature of 250°C and a high-frequency power of 20
W was then applied under a pressure of 5×10^{-3} Torr to
form an X-ray permeable film 132 of silicon nitride
15 having a thickness of 2 μ m.

A gold film having a thickness of 500 Å which
would be a plating electrode 134 for the formation of
an X-ray absorber and a chromium film having a
thickness of 50 Å as a metal thin film 133 for adhesion
20 were continuously deposited by an EB vapor deposition,
as shown in Fig. 15A. A material of the metal thin
film 133 is a metal capable of improving adhesive
strength such as Ti, Al or Zn. An electron rays resist
PMMA (trade name OEER-1000, made by Tokyo Oka Kogyo
25 Co., Ltd.) was applied thereonto, and a desired fine
resist pattern 135 was then formed by means of an
electron rays depictor, as shown in Fig. 15B.

1 Next, plating was carried out at 50°C at a
current density of 1 mA/cm² by the use of a gold sulfite
plating solution (trade name Neutronex 309, made by
EEJA) to form a gold film which would be an X-ray
5 absorber 136 and an alignment mark 137. Afterward, the
resist pattern 135 was peeled off with an exclusive
peeling solution, as shown in Fig. 15C.

 The portion of the plating electrode 134 on
which the X-ray absorber 136 and the alignment mark 137
10 were not formed was peeled by means of an RIE
equipment. After back pressure was reduced to 1×10^{-5}
Torr, 20 sccm of an argon gas was fed thereto and 200 W
was then applied under a pressure of 5×10^{-2} Torr to
carry out etching. Since the plating electrode 134,
15 the X-ray absorber 136 and the alignment mark 137 were
all made of gold, they were equally etched, so that the
X-ray absorber and the alignment mark took the
conformations of 136' and 137', as shown in Fig. 15D.

 A protective film 138 was then formed on a
20 circuit pattern portion by the use of a novolak resist
(trade name AZ-1370SF, made by Tokyo Oka Kogyo Co.,
Ltd.), as shown in Fig. 15E. Furthermore, 20 sccm of
an oxygen gas was fed to the RIE equipment, and 200 W
was then applied under a pressure of 5×10^{-2} Torr, with
25 the result that the portion of the metal thin film 133
on a scribe line having no alignment mark thereon was
oxidized with oxygen plasma to form a chromium oxide

1 film 139, as shown in Fig. 15F.

Afterward, the protective film 138 was peeled off with an exclusive peeling solution, as shown in Fig. 15G. Alternatively, an inorganic film of SiO_2 or
5 the like may be formed as the protective film 138 by sputtering or the like, and it may be maintained as the protective film for the X-ray mask. In the last place, the back of the Si wafer was etched at 110°C with a 3% by weight aqueous potassium hydroxide solution to form
10 a supporting frame 131, as shown in Fig. 15H. Fig. 15I shows a plan view of the constitution of Fig. 15H.

In such an X-ray mask structure as in Fig. 15H, the portion of the metal thin film for adhesion of chromium on the scribe line on which the alignment mark
15 was not formed was only oxidized without etching, and therefore there could be prevented the thickness reduction of the gold film which was the X-ray absorber 136', the generation of the film thickness ununiformity of silicon nitride constituting the X-ray permeable
20 film on the scribe line, and the damage of the film surface. This X-ray mask structure was set on an exposure chamber 8 (Fig. 18), and alignment was then carried out by the use of alignment light from an He-Ne laser (633 nm). As a result, a stable alignment light
25 permeability could be obtained, and the highly precise alignment could be attained. In addition, when exposed to the X rays, the thickness of the X-ray absorber was

1 not decreased, so that a sufficient contrast could be
obtained. In consequence, a highly precise
semiconductor chip could be prepared.

Example 13

5 Figs. 16A to 16H illustrate as sectional views
the thirteenth example of an X-ray mask structure
manufacturing process according to the present
invention.

As a material of a substrate 141 which will be
10 a supporting frame, an Si wafer is often used, and in
this example, an Si wafer having a diameter of 3 inches
and a thickness of 2 mm was used. This substrate was
set on a plasma CVD equipment. In the first place,
back pressure was reduced to 2×10^{-6} Torr, and 5 sccm
15 of a 10% silane gas diluted with hydrogen and 20 sccm
of an ammonia gas were fed through a hole perforated in
a lower electrode. The substrate 141 was heated up to
a temperature of 350°C and a high-frequency power of 20
W was then applied under a pressure of 5×10^{-3} Torr to
20 form an X-ray permeable film 142 of silicon nitride
having a thickness of 2 μm .

A gold film having a thickness of 500 Å which
would be a plating electrode 144 for the formation of
an X-ray absorber and a titanium film having a
25 thickness of 50 Å as a metal thin film 143 for adhesion
were continuously deposited by an EB vapor deposition,
as shown in Fig. 16A. Next, the back of the Si wafer

1 was etched at 110°C with a 30% by weight aqueous
potassium hydroxide solution to form a supporting frame
141, as shown in Fig. 16B. An electron rays resist
PMMA (trade name OEER-1000, made by Tokyo Oka Kogyo
5 Co., Ltd.) was applied thereonto, and a desired fine
resist pattern 145 was then formed by means of an
electron rays depictor, as shown in Fig. 16C.

Next, plating was carried out at 50°C at a
current density of 1 mA/cm² by the use of a gold sulfite
10 plating solution (trade name Neutronex 309, made by
EEJA) to form a gold film which would be an X-ray
absorber 146 and an alignment mark 147. Afterward, the
resist pattern 145 was peeled off with an exclusive
peeling solution, as shown in Fig. 16D.

15 The portion of the plating electrode 144 on
which the X-ray absorber 146 and the alignment mark 147
were not formed was peeled by means of an RIE
equipment. After back pressure was reduced to 1×10^{-5}
Torr, 20 sccm of an argon gas was fed thereto and 200 W
20 was then applied under a pressure of 5×10^{-2} Torr to
carry out etching. Since the plating electrode 144,
the X-ray absorber and the alignment mark were all made
of gold, they were equally etched, so that the X-ray
absorber and the alignment mark took the conformations
25 of 146' and 147', as shown in Fig. 16E. A protective
film 148 was then formed on a circuit pattern portion
by the use of a novolak resist (trade name AZ-1370SF,

1 made by Tokyo Oka Kogyo Co., Ltd.), as shown in Fig.
16F.

Furthermore, a heat treatment was carried out
at 100°C in an oxygen atmosphere, and a region of the
5 metal thin film 143 on which the alignment mark was not
formed and which would be used for the alignment was
oxidized to form a titanium oxide film 149, as shown in
Fig. 16G. The protective film 148 was peeled off with
an exclusive peeling solution, as shown in Fig. 16H.
10 Alternatively, an inorganic film of SiO_2 or the like may
be formed as the protective film 148 by sputtering or
the like, and it may be maintained as the protective
film for the X-ray mask.

As described above, the region of the metal
15 thin film of chromium for adhesion on which the
alignment mark was not formed and which would be used
for the alignment was oxidized without etching, and
therefore there could be prevented the thickness
reduction of the gold film which was the X-ray absorber
20 146', the generation of film thickness ununiformity in
the range of silicon nitride constituting the X-ray
permeable film which would be used for the alignment,
and the damage of the film surface. As in Example 12,
this X-ray mask structure was set on an exposure
25 chamber, and alignment was then carried out by the use
of alignment light from an He-Ne laser (633 nm). As a
result, a stable alignment light permeability could be

1 obtained, and the highly precise alignment could be
attained. In addition, when exposed to the X rays, the
thickness of the X-ray absorber was not decreased, so
that a sufficient contrast could be obtained. In
5 consequence, a highly precise semiconductor chip could
be prepared.

Example 14

Figs. 17A to 17E illustrate as sectional views
the fourteenth example of an X-ray mask structure
10 manufacturing process according to the present
invention.

As a material of a substrate 151 which would be
a supporting frame, an Si wafer was used. A silicon
nitride film having a thickness of 2 μm was formed as
15 an X-ray permeable film 152 in the same manner as in
Example 13.

A nickel film having a thickness of 20 nm as a
metal thin film 153 which would be a plating electrode
for the formation of an X-ray absorber was deposited by
20 an EB vapor deposition, as shown in Fig. 17A. An
electron rays resist PMMA (trade name OEER-1000, made
by Tokyo Oka Kogyo Co., Ltd.) was applied thereonto,
and a desired fine resist pattern 155 was then formed
by means of an electron rays depictor, as shown in Fig.
25 17B.

Next, plating was carried out at 50°C at a
current density of 0.5 mA/cm² by the use of a gold

1 sulfite plating solution (trade name Neutronex 309,
made by EEJA) to form a gold film which would be an X-
ray absorber 156. Afterward, the resist pattern 155
was peeled off with an exclusive peeling solution, as
5 shown in Fig. 17C. Afterward, the back of the Si wafer
was etched at 110°C with a 30% by weight aqueous
potassium hydroxide solution to form a supporting frame
151, as shown in Fig. 17D.

In the last place, in a focusing ion injector,
10 oxygen ions were injected at an oxygen ion
concentration of 10^{16} - 10^{17} ions/cm² at 40-50 KV, whereby
a region of the metal thin film 153 on which the
alignment mark was not formed and which would be used
for the alignment was converted into nickel oxide 159,
15 as shown in Fig. 17E. The utilization of the focusing
ion injector technique permits omitting the preparation
and the peeling of a protective film. Furthermore,
when the ion injection is used at the suitably selected
ion concentration and accelerating voltage, even the
20 relatively thick film can be oxidized. Therefore, the
metal thin film may be formed so that nickel oxide may
have such a thickness as to become a reflection
preventing film (690 Å in the case of an He-Ne laser).

As described above, the region of the metal
25 thin film of nickel on which the alignment mark was not
formed and which would be used for the alignment was
oxidized without peeling, and therefore there could be

1 prevented the thickness reduction of the gold film
which was the X-ray absorber 156, the generation of
film thickness ununiformity in the range of silicon
nitride constituting the X-ray permeable film which
5 would be used for the alignment, and the damage of the
film surface. As in Example 12, this X-ray mask
structure was set on an exposure chamber, and alignment
was then carried out by the use of alignment light from
an He-Ne laser (633 nm). As a result, a stable
10 alignment light permeability could be obtained, and the
highly precise alignment could be attained. In
addition, when exposed to the X rays, the thickness of
the X-ray absorber was not decreased, so that a
sufficient contrast could be obtained. In consequence,
15 a highly precise semiconductor chip could be prepared.

20

25



1 WHAT IS CLAIMED IS:

1. An X-ray mask structure comprising an X-ray
absorber having a desired pattern, an X-ray permeable
film supporting the X-ray absorber, and a supporting
5 frame for supporting the X-ray permeable film,

said X-ray mask structure being characterized
in that a metal oxide film is formed on the portion of
the X-ray permeable film having no X-ray absorber
thereon.

10

2. The X-ray mask structure according to Claim
1 wherein the metal oxide film has a thickness of 8 Å
to 1000 Å.

15

3. The X-ray mask structure according to Claim
1 wherein the metal oxide film comprises an oxide of a
metal having an atomic number of 35 or less.

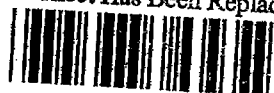
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4. The X-ray mask structure according to Claim
3 wherein the metal is at least one selected from the
group consisting of chromium, titanium, aluminum, zinc,
copper and nickel.

25

5. The X-ray mask structure according to Claim
3 wherein the X-ray absorber has an oxide film of a
metal having an atomic number of 70 or more.

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1 6. The X-ray mask structure according to Claim
5 wherein the metal having an atomic number of 70 or
more is at least one selected from the group consisting
of tantalum, tungsten, platinum, gold and lead.

5

 7. The X-ray mask structure according to Claim
1 wherein an intermediate layer is formed between the
X-ray permeable film and the X-ray absorber, and the
metal oxide film is an oxide of a metal constituting
10 the intermediate layer.

 8. The X-ray mask structure according to Claim
7 wherein the metal oxide film has a thickness of 8 Å
to 1000 Å.

15

 9. The X-ray mask structure according to Claim
7 wherein the metal oxide film comprises an oxide of a
metal having an atomic number of 35 or less.

20 10. The X-ray mask structure according to
Claim 9 wherein the metal is at least one selected from
the group consisting of chromium, titanium, aluminum,
zinc, copper and nickel.

25 11. The X-ray mask structure according to
Claim 9 wherein the X-ray absorber has an oxide film of
a metal having an atomic number of 70 or more.



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1 12. The X-ray mask structure according to
Claim 11 wherein the metal having an atomic number of
70 or more is at least one selected from the group
consisting of tantalum, tungsten, platinum, gold and
5 lead.

13. An X-ray mask structure comprising an X-
ray absorber having a desired pattern, an alignment
mark, an X-ray permeable film supporting the X-ray
10 absorber and the mark, and a supporting frame for
supporting the X-ray permeable film,

said X-ray mask structure being characterized
in that a metal oxide film is formed on at least the
portion of the X-ray permeable film in the vicinity of
15 the mark and having no X-ray absorber thereon.

14. The X-ray mask structure according to
Claim 13 wherein the alignment mark is formed on the
metal oxide film.

20

15. The X-ray mask structure according to
Claim 13 wherein the metal oxide film is formed on the
portion of the X-ray permeable film having no alignment
mark
25 thereon.

16. The X-ray mask structure according to

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1 Claim 13 wherein the metal oxide film has a thickness
of 8 Å to 1000 Å.

17. The X-ray mask structure according to
5 Claim 13 wherein the metal oxide film comprises an
oxide of a metal having an atomic number of 35 or less.

18. The X-ray mask structure according to
Claim 17 wherein the metal is at least one selected
10 from the group consisting of chromium, titanium,
aluminum, zinc, copper and nickel.

19. The X-ray mask structure according to
Claim 17 wherein the X-ray absorber has an oxide film
15 of a metal having an atomic number of 70 or more.

20. The X-ray mask structure according to
Claim 19 wherein the metal having an atomic number of
70 or more is at least one selected from the group
20 consisting of tantalum, tungsten, platinum, gold and
lead.

21. The X-ray mask structure according to
Claim 13 wherein an intermediate layer is formed
25 between the X-ray absorber and the X-ray permeable
film, and between the alignment mark and the X-ray
permeable film.

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1 22. The X-ray mask structure according to
Claim 21 wherein the metal oxide film has a thickness
of 8 Å to 1000 Å.

5 23. The X-ray mask structure according to
Claim 21 wherein the metal oxide film comprises an
oxide of a metal having an atomic number of 35 or less.

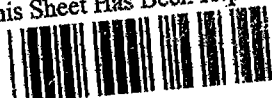
10 24. The X-ray mask structure according to
Claim 23 wherein the metal is at least one selected
from the group consisting of chromium, titanium,
aluminum, zinc, copper and nickel.

15 25. The X-ray mask structure according to
Claim 23 wherein the X-ray absorber has an oxide film
of a metal having an atomic number of 70 or more.

20 26. The X-ray mask structure according to
Claim 25 wherein the metal having an atomic number of
70 or more is at least one selected from the group
consisting of tantalum, tungsten, platinum, gold and
lead.

25 27. An X-ray exposing method which comprises
the step of irradiating a material to be exposed with X
rays through an X-ray mask structure described in any
one of Claims 1 to 26.

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1 28. An X-ray exposing method which comprises
the step of irradiating a material to be exposed with X
rays through an X-ray mask structure described in any
one of Claims 1 to 26, after alignment is carried out
5 between the mask structure and the material to be
exposed.

 29. A semiconductor device manufactured by
irradiating a material to be exposed with X rays
10 through an X-ray mask structure described in any one of
Claims 1 to 26 to form a circuit pattern on the
material to be exposed.

 30. A semiconductor device manufactured by
15 irradiating a material to be exposed with X rays
through an X-ray mask structure described in any one of
Claims 1 to 26, after alignment is carried out between
the mask structure and the material to be exposed,
thereby forming a circuit pattern on the material to be
20 exposed.

 31. A method for manufacturing an X-ray mask
structure comprising an X-ray absorber having a desired
pattern, an X-ray permeable film supporting the X-ray
25 absorber, and a supporting frame for supporting the X-
ray-permeable film, said method being characterized by
having a process in which after the formation of an X-

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1 ray absorber pattern, the portion of the X-ray
permeable film having no X-ray absorber pattern thereon
is subjected to an oxidation treatment.

5 32. The method for manufacturing an X-ray mask
structure according to Claim 31 wherein the oxidation
treatment is an oxygen plasma treatment.

33. The method for manufacturing an X-ray mask
10 structure according to Claim 31 wherein the oxidation
treatment is an oxygen ion injection treatment.

34. The method for manufacturing an X-ray mask
structure according to Claim 31 wherein the oxidation
15 treatment is a heat treatment in an oxygen atmosphere.

35. The method for manufacturing an X-ray mask
structure according to Claim 31 which has a process in
which the surface of the X-ray absorber pattern is
20 subjected to an oxidation treatment.

36. The method for manufacturing an X-ray mask
structure according to Claim 35 wherein the oxidation
treatment is an oxygen plasma treatment.
25

37. The method for manufacturing an X-ray mask
structure according to Claim 35 wherein the oxidation

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1 treatment is an oxygen ion injection treatment.

38. The method for manufacturing an X-ray mask
structure according to Claim 35 wherein the oxidation
5 treatment is a heat treatment in an oxygen atmosphere.

39. The method for manufacturing an X-ray mask
structure according to Claim 35 wherein the oxidation
treatment of the X-ray permeable film and the oxidation
10 treatment of the X-ray absorber are carried out in one
process.

40. A method for manufacturing an X-ray mask
structure comprising an X-ray absorber having a desired
15 pattern, an X-ray permeable film supporting the X-ray
absorber, and a supporting frame for supporting the X-
ray permeable film, said method being characterized by
having

- (a) a process for forming a metal film on the X-ray
20 permeable film,
- (b) a process for forming an X-ray absorber pattern on
the metal film, and
- (c) a process in which after the formation of the X-
ray absorber pattern, the portion of the metal film
25 having no X-ray absorber pattern thereon is subjected
to an oxidation treatment.

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1 41. The method for manufacturing an X-ray mask
structure according to Claim 40 wherein the oxidation
treatment is an oxygen plasma treatment.

5 42. The method for manufacturing an X-ray mask
structure according to Claim 40 wherein the oxidation
treatment is an oxygen ion injection treatment.

10 43. The method for manufacturing an X-ray mask
structure according to Claim 40 wherein the oxidation
treatment is a heat treatment in an oxygen atmosphere.

15 44. The method for manufacturing an X-ray mask
structure according to Claim 40 which has a process in
which the surface of the X-ray absorber pattern is
subjected to an oxidation treatment.

20 45. The method for manufacturing an X-ray mask
structure according to Claim 44 wherein the oxidation
treatment is an oxygen plasma treatment.

25 46. The method for manufacturing an X-ray mask
structure according to Claim 44 wherein the oxidation
treatment is an oxygen ion injection treatment.

 47. The method for manufacturing an X-ray mask
structure according to Claim 44 wherein the oxidation

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1 treatment is a heat treatment in an oxygen atmosphere.

48. The method for manufacturing an X-ray mask
structure according to Claim 44 wherein the oxidation
5 treatment of the metal film on the X-ray permeable film
and the oxidation treatment of the X-ray absorber are
carried out in one process.

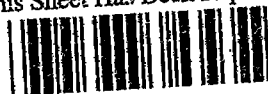
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1 ABSTRACT OF THE DISCLOSURE

 An X-ray mask structure comprises an X-ray
absorber having a desired pattern, an X-ray permeable
film supporting the X-ray absorber, and a supporting
5 frame for supporting the X-ray permeable film. The X-
ray mask structure has a metal oxide film formed on the
portion of the X-ray permeable film having no X-ray
absorber thereon.

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FIG.1A

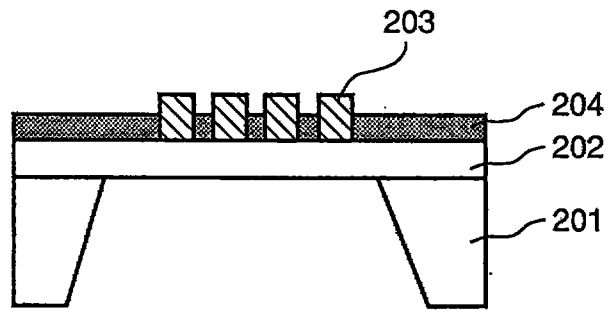


FIG.1B

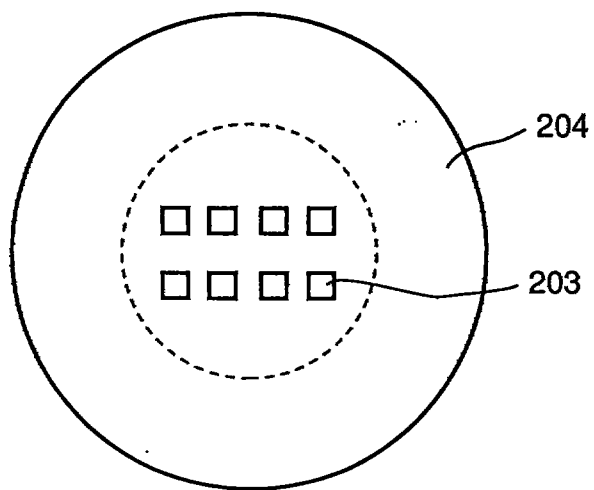


FIG.2

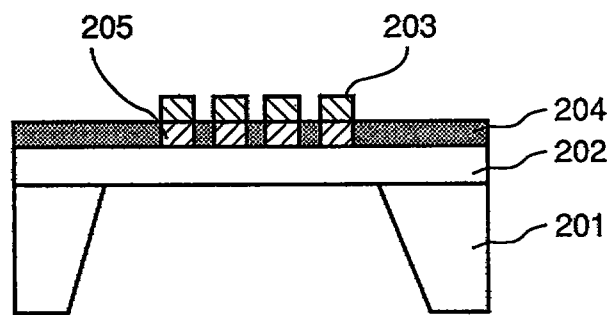


FIG.3A

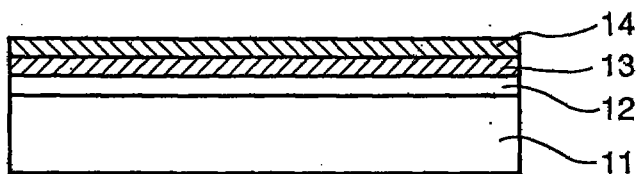


FIG.3B

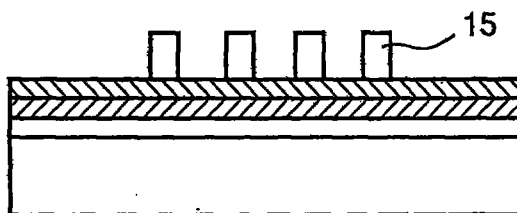


FIG.3C

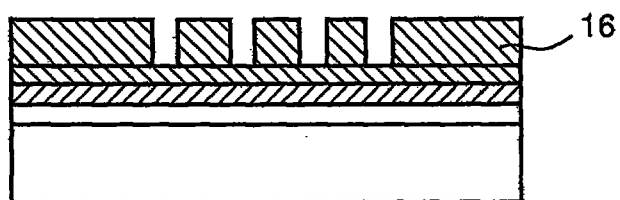


FIG.3D

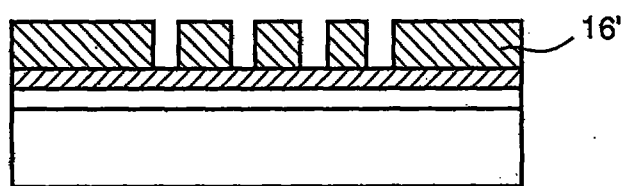


FIG.3E

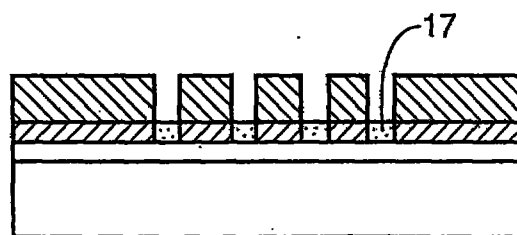


FIG.3F

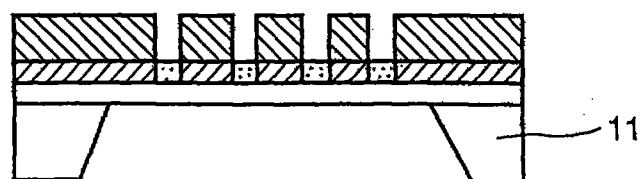


FIG.4

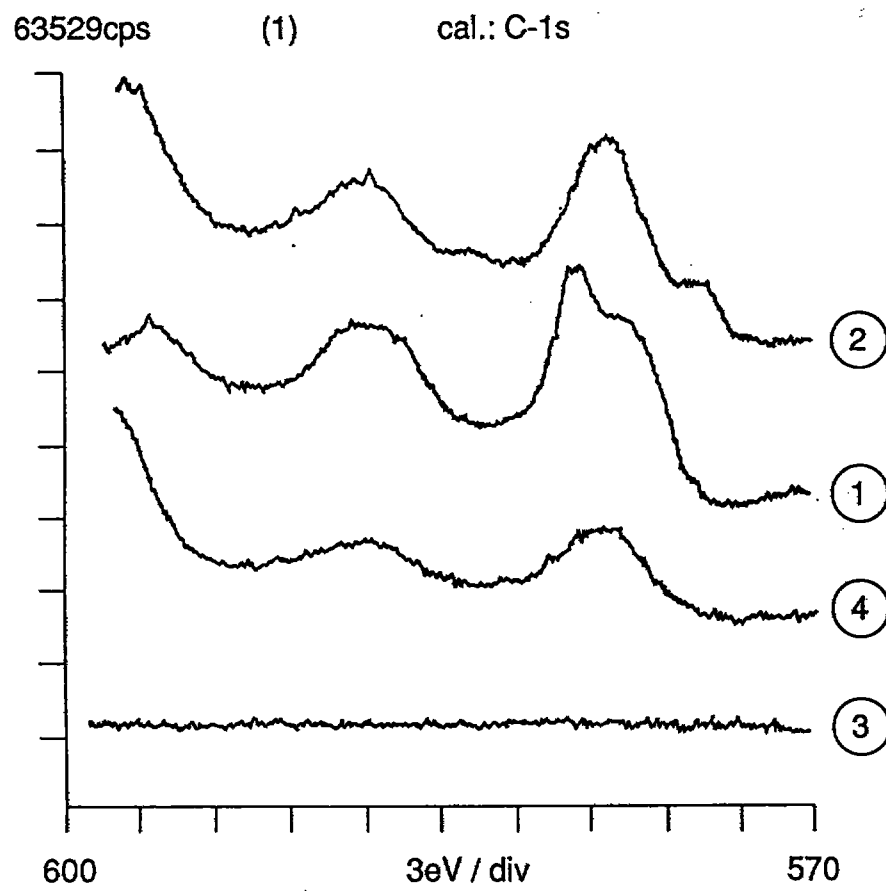


FIG.5A

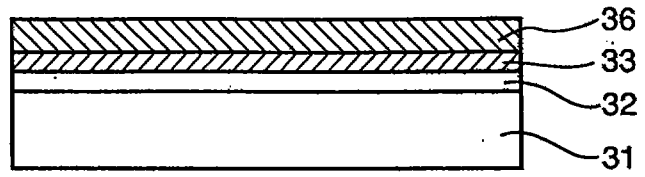


FIG.5B

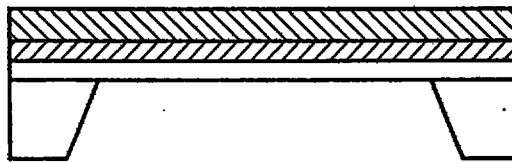


FIG.5C

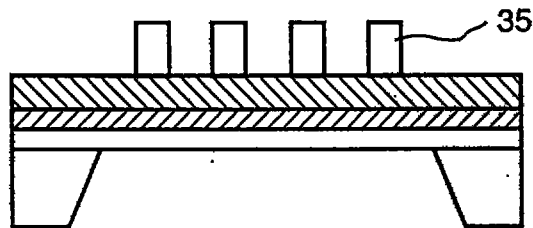


FIG.5D

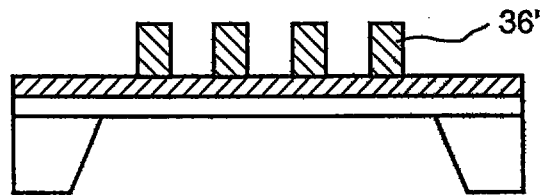


FIG.5E

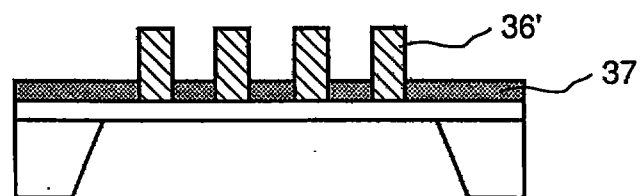


FIG.6A

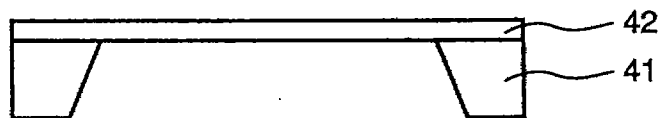


FIG.6B

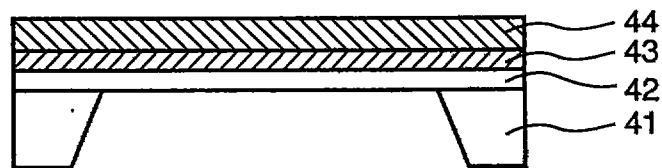


FIG.6C

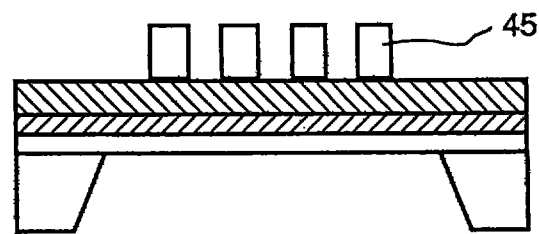


FIG.6D

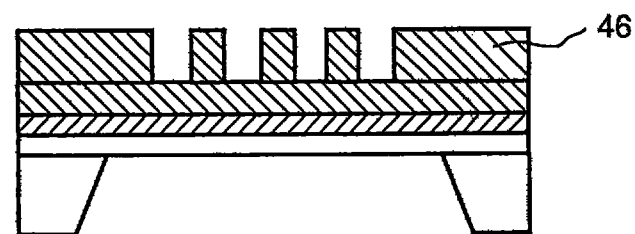


FIG.6E

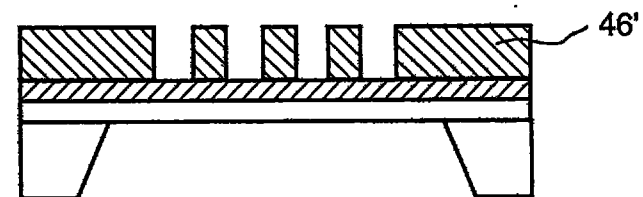


FIG.6F

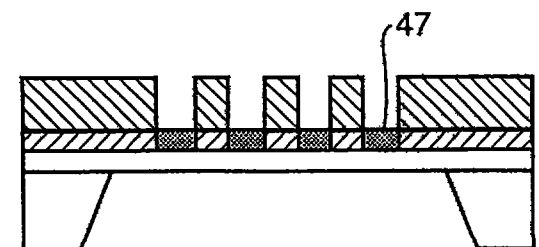


FIG.7A

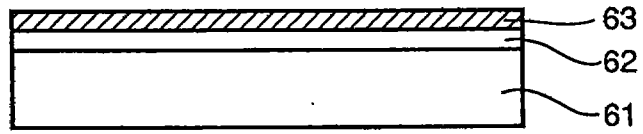


FIG.7B

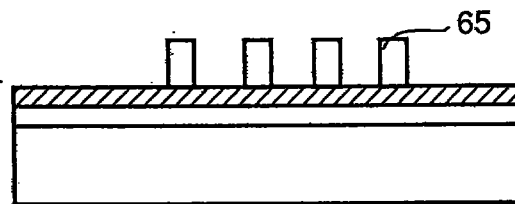


FIG.7C

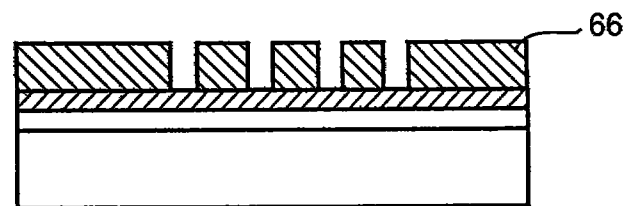


FIG.7D

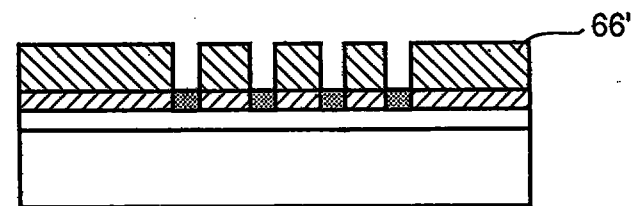


FIG.7E

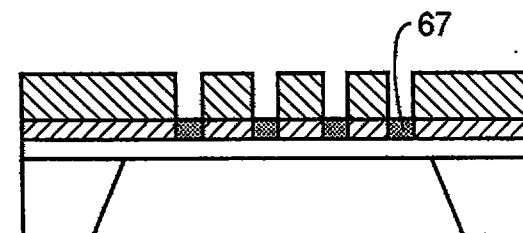


FIG.8A

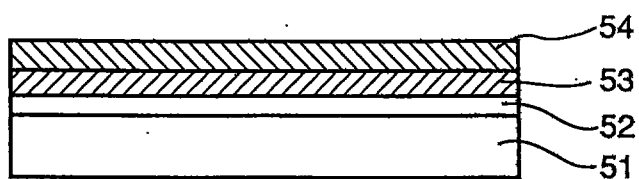


FIG.8B

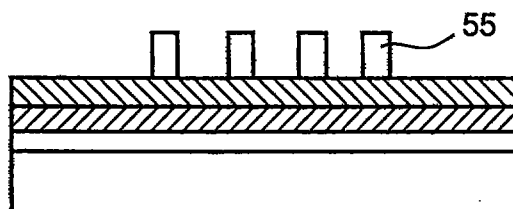


FIG.8C

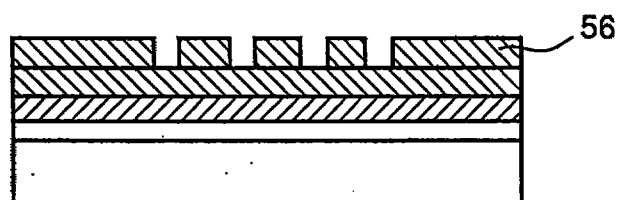


FIG.8D

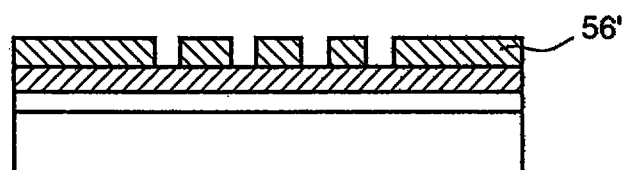


FIG.8E

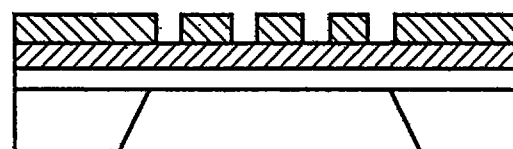


FIG.8F

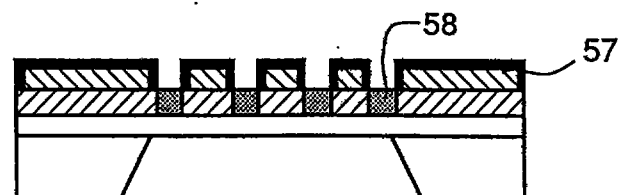


FIG.9A

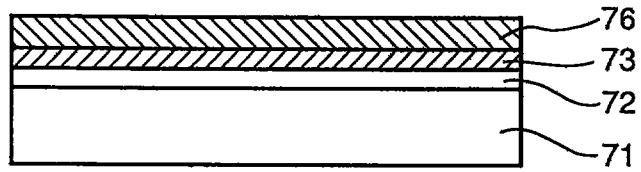


FIG.9B

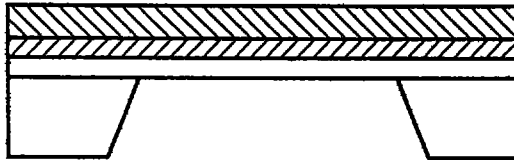


FIG.9C

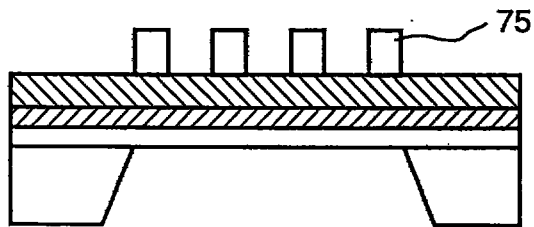


FIG.9D

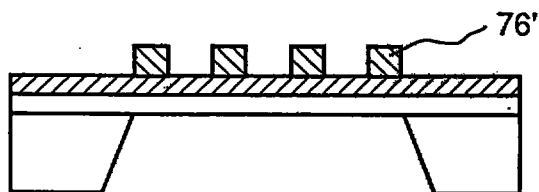


FIG.9E

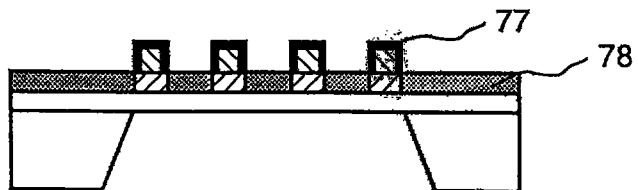


FIG.10A

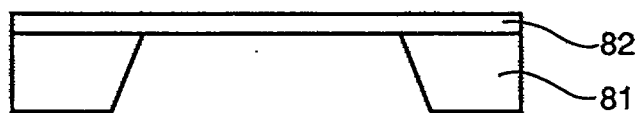


FIG.10B

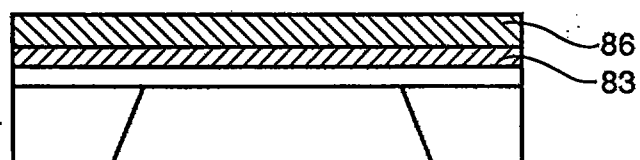


FIG.10C

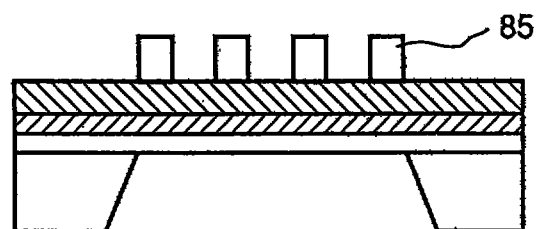


FIG.10D

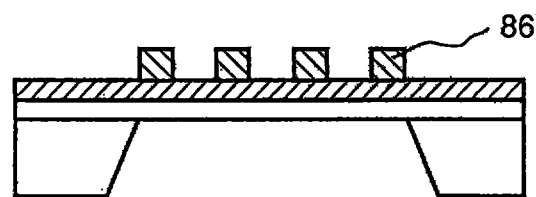
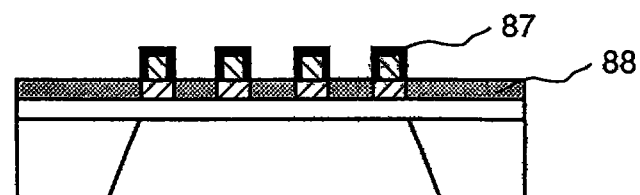
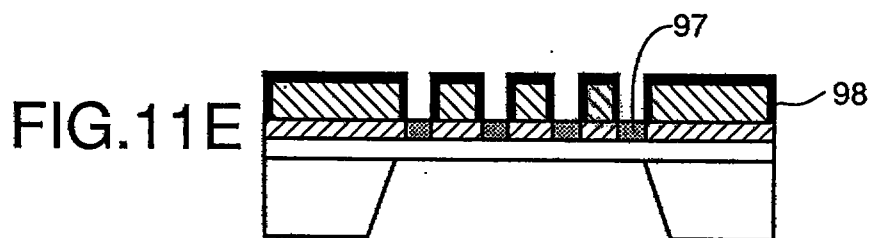
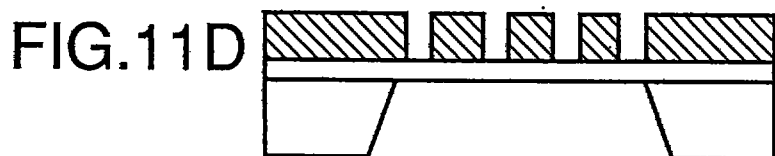
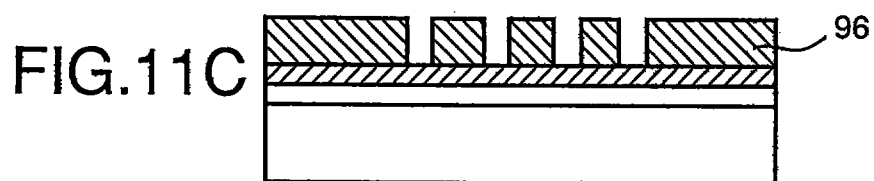
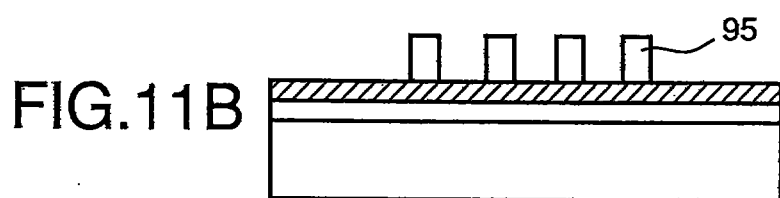
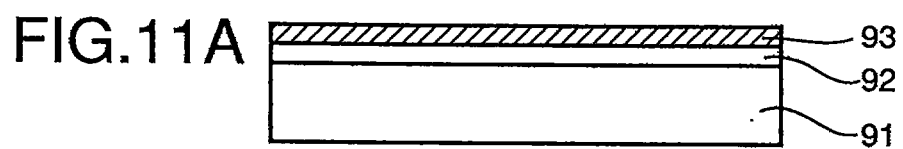
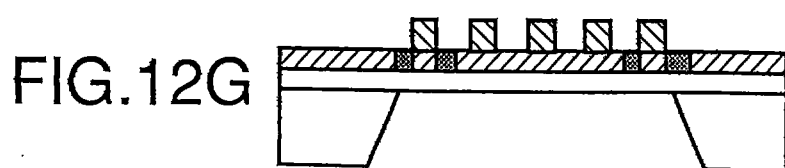
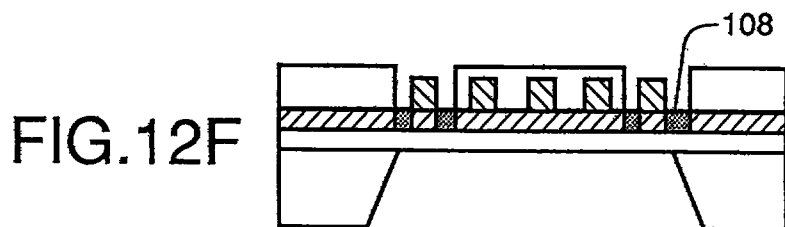
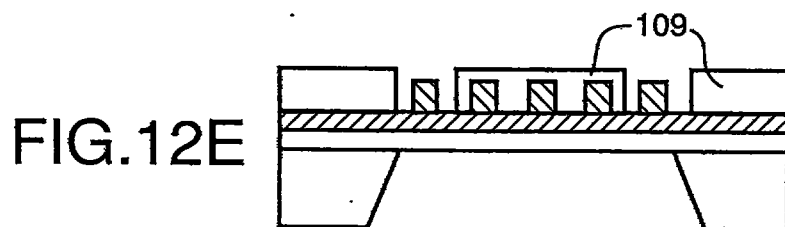
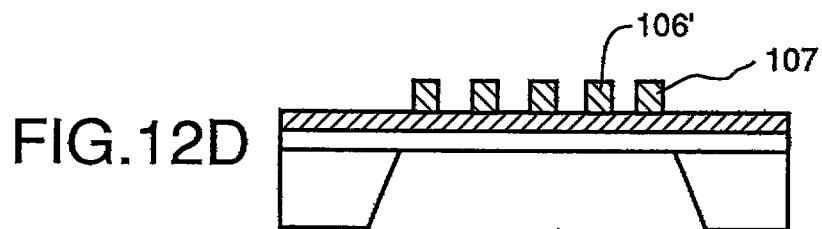
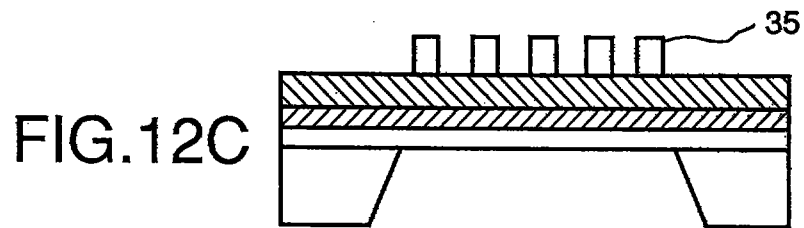
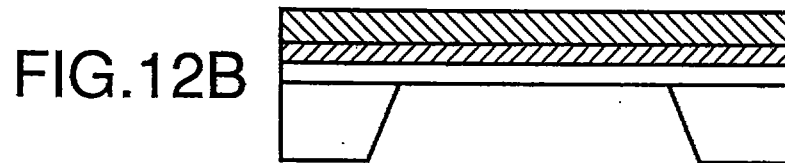
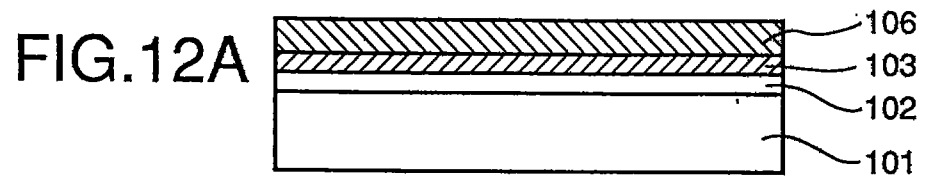
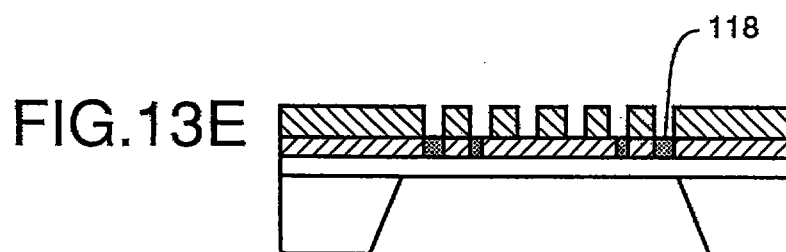
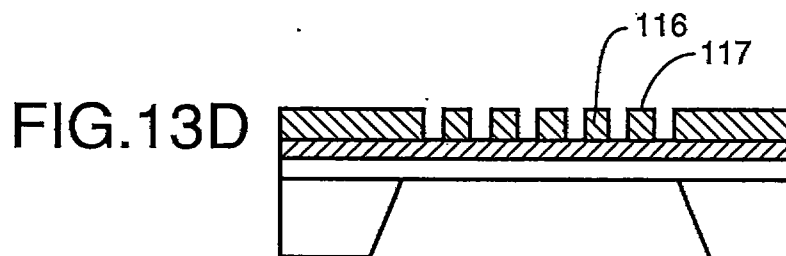
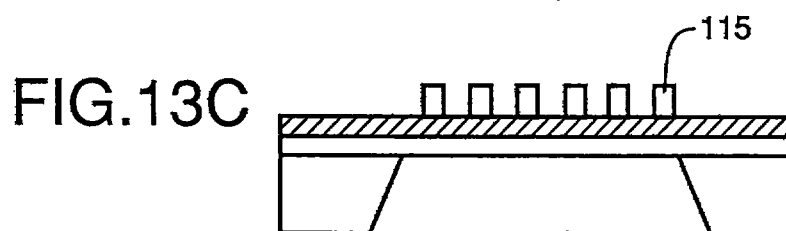
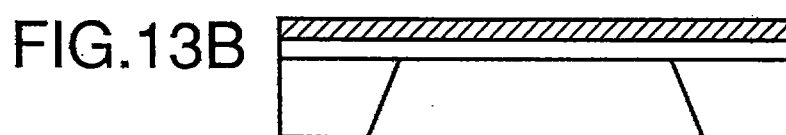
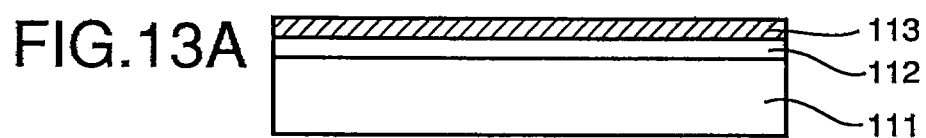


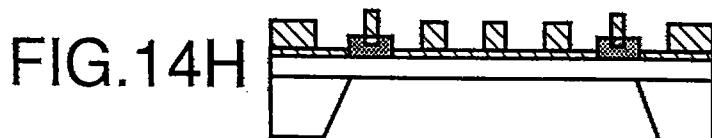
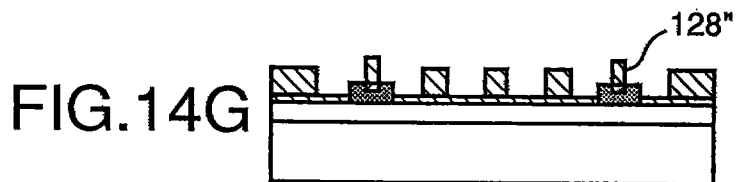
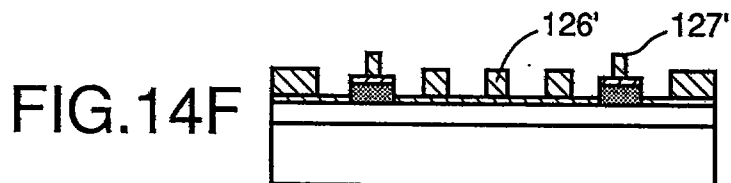
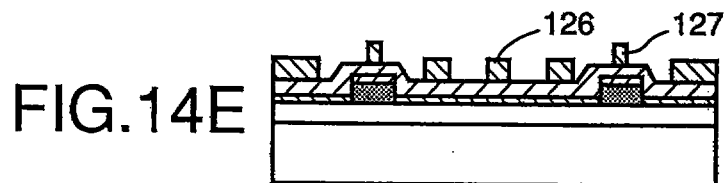
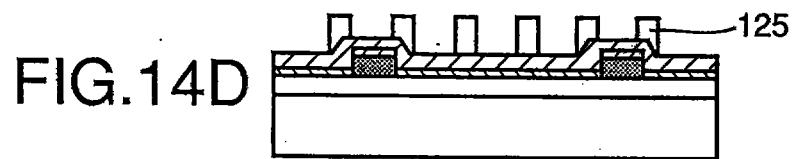
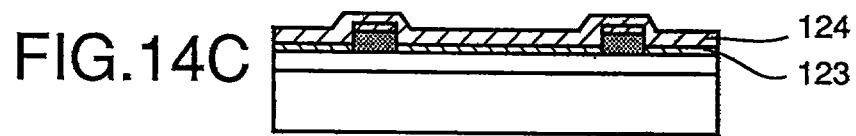
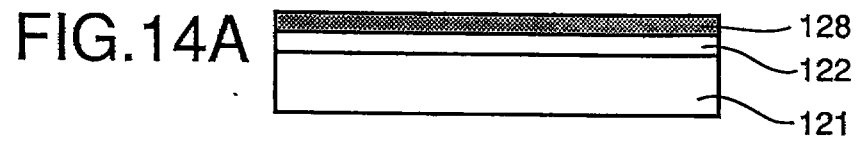
FIG.10E

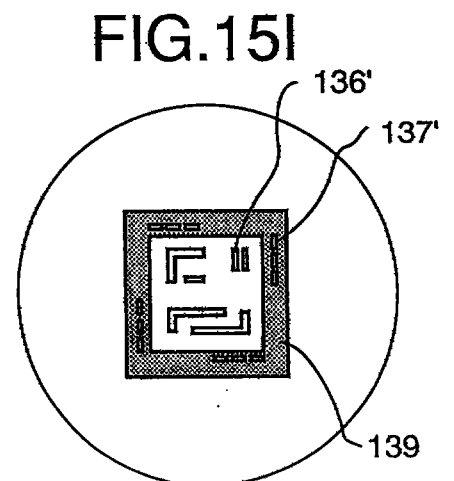
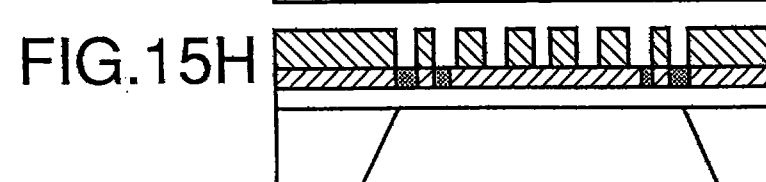
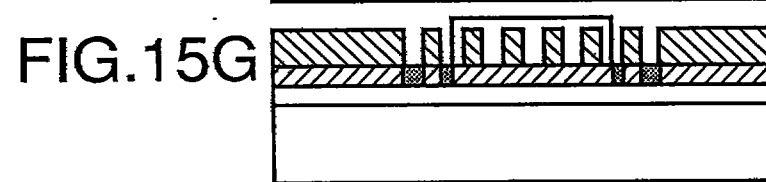
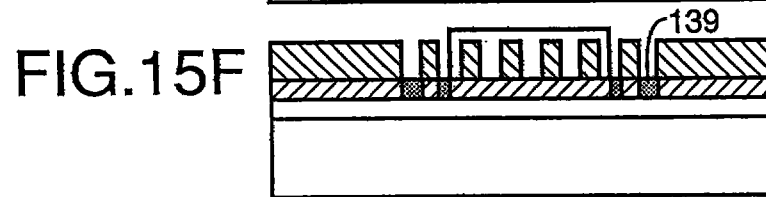
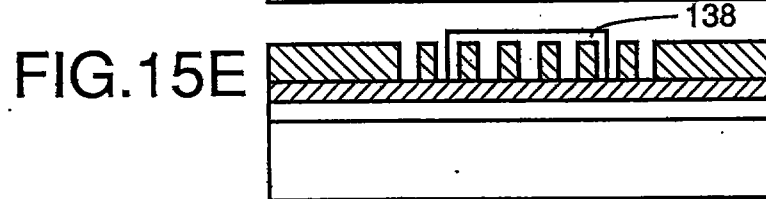
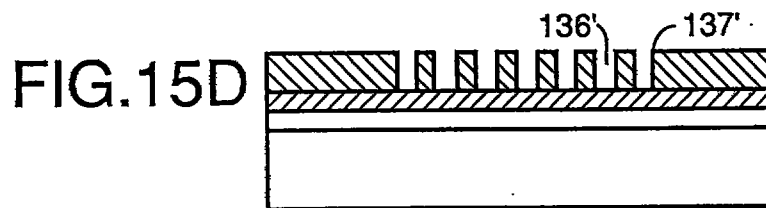
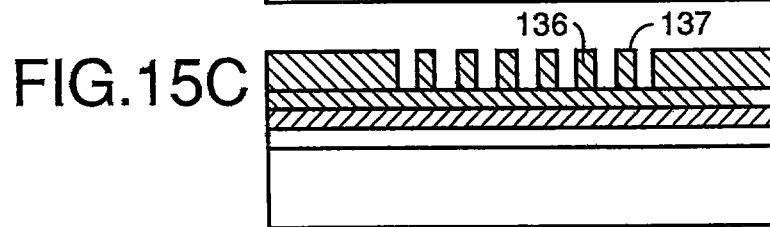
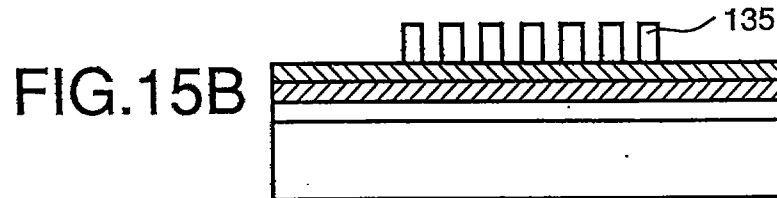
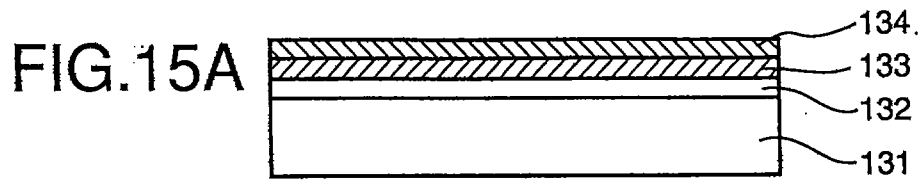


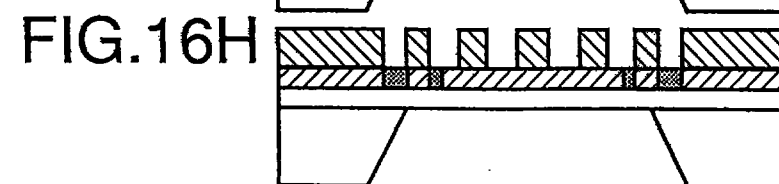
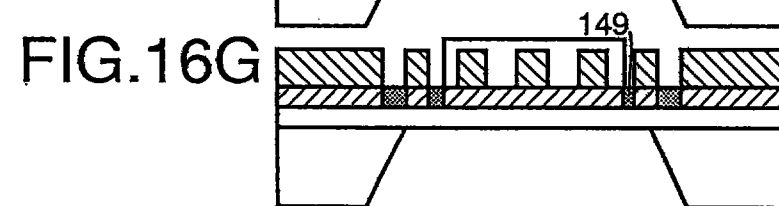
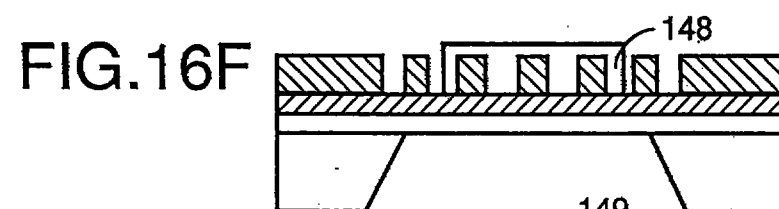
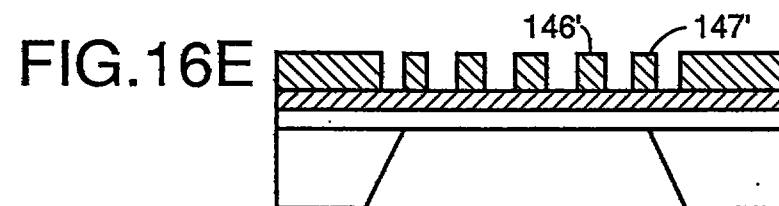
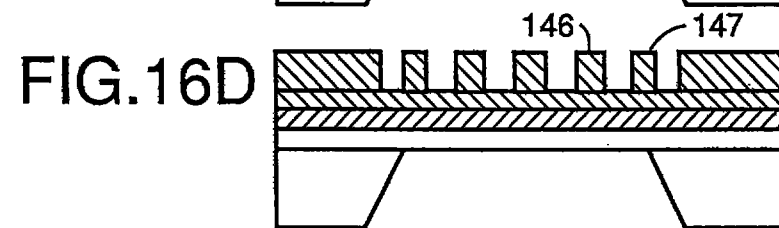
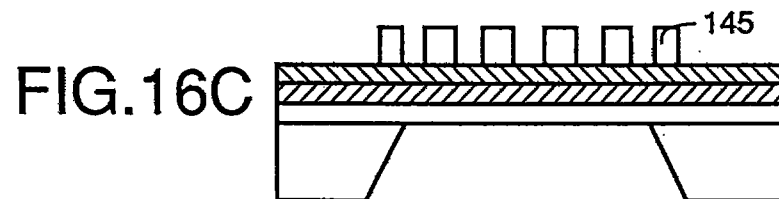
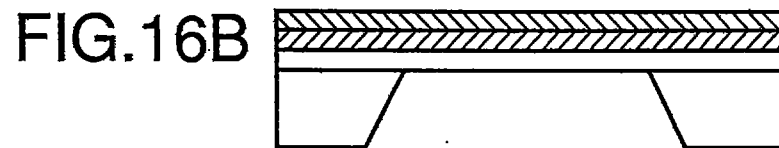
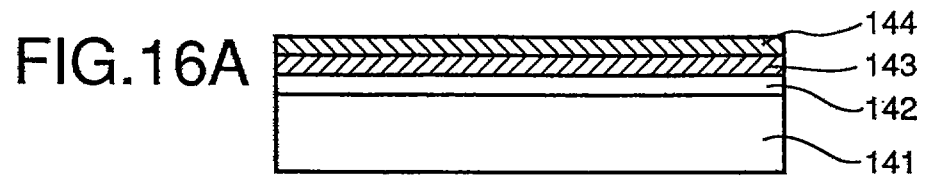












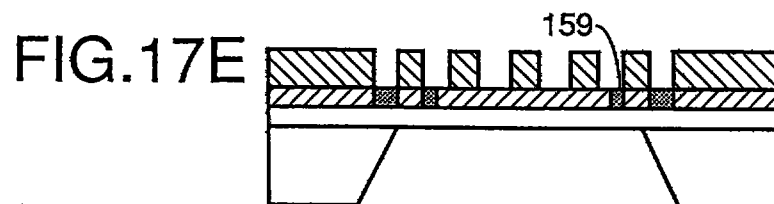
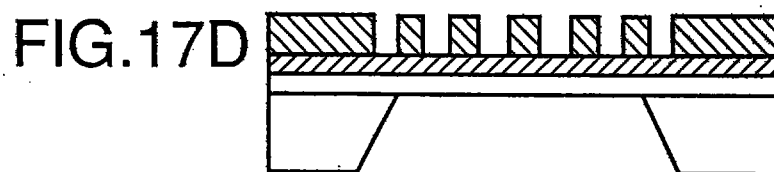
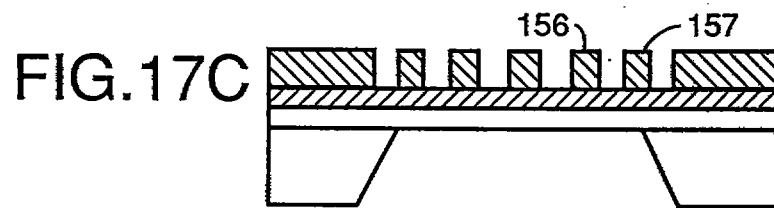
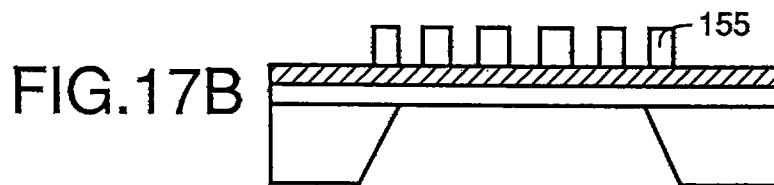
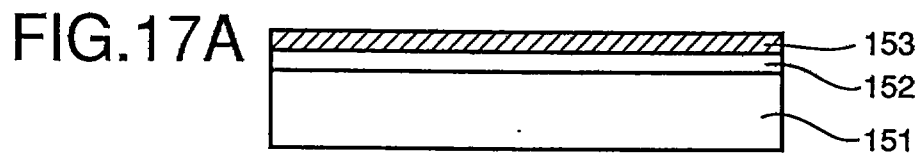
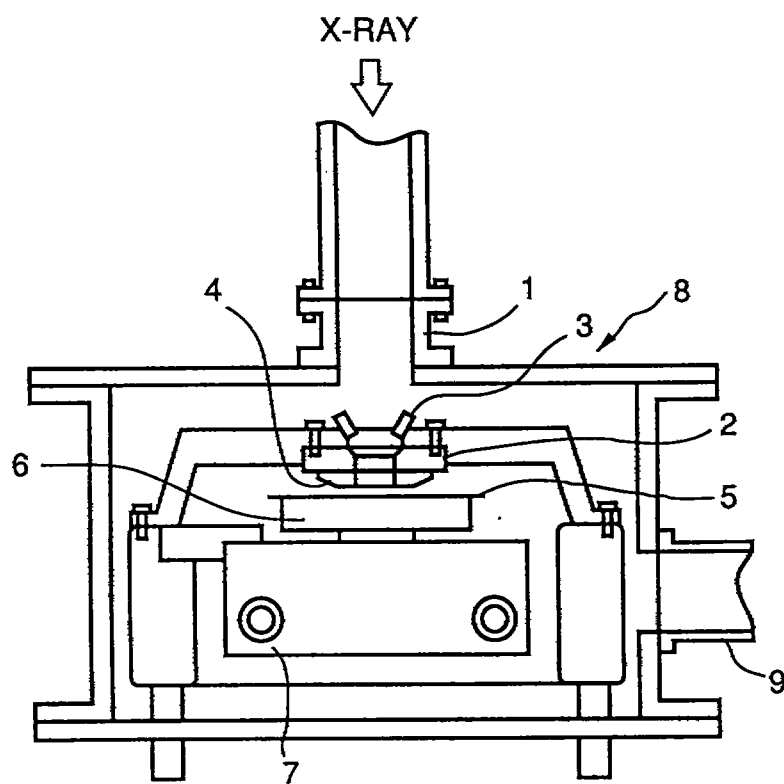
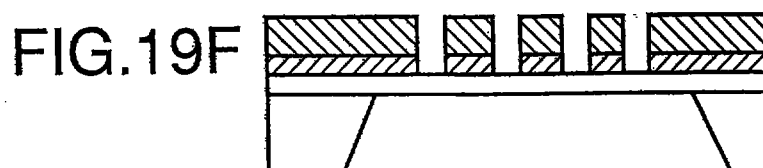
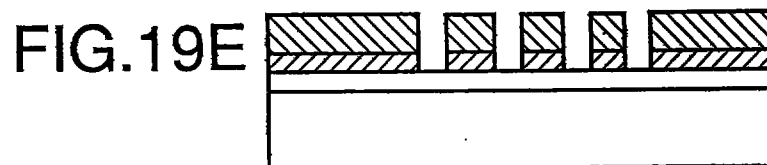
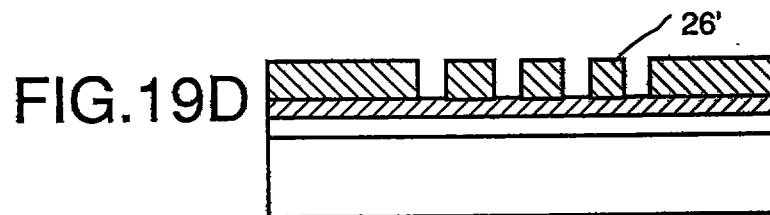
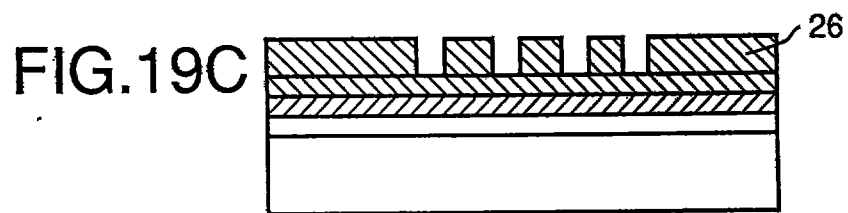
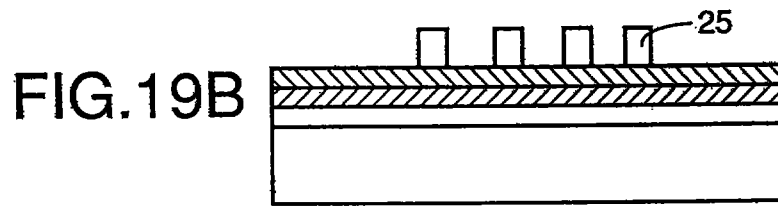
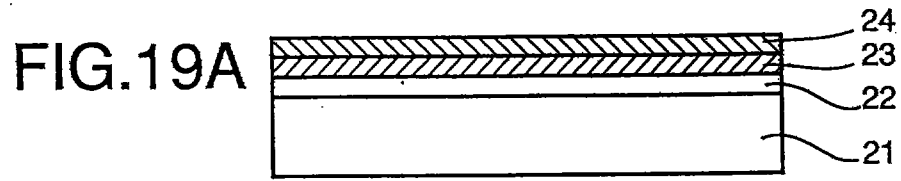


FIG.18





3-A000000

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X-RAY MASK STRUCTURE AND X-RAY EXPOSING METHOD, AND
SEMICONDUCTOR DEVICE MANUFACTURED BY USE OF X-RAY MASK
STRUCTURE, AND METHOD FOR MANUFACTURING X-RAY MASK
STRUCTURE

1 ABSTRACT OF THE DISCLOSURE

An X-ray mask structure comprises an X-ray
absorber having a desired pattern, an X-ray permeable
film supporting the X-ray absorber, and a supporting
5 frame for supporting the X-ray permeable film. The X-
ray mask structure has a metal oxide film formed on the
portion of the X-ray permeable film having no X-ray
absorber thereon.

10

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REPLACED

REPLACEMENT SHEET

13 MAR 1997

This Sheet Has Been Replaced





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What is claimed is:

1. An X-ray mask structure comprising:
an X-ray absorber having a masking pattern;
an X-ray permeable film for supporting the X-ray absorber on one surface of the X-ray permeable film;
a supporting frame for supporting the X-ray permeable film; and
a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon.
2. The X-ray mask structure according to claim 1, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.
3. The X-ray mask structure according to claim 1, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.
4. The X-ray mask structure according to claim 3, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.
5. The X-ray mask structure according to claim 3, wherein the X-ray absorber has an oxide film of a metal having an atomic number of 70 or more.
6. The X-ray mask structure according to claim 5, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, Tungsten, platinum, gold and lead.
7. The X-ray mask structure according to claim 1, wherein an intermediate layer is formed between the X-ray permeable film and the X-ray absorber, and the metal oxide film is an oxide of a metal constituting the intermediate layer.
8. The X-ray mask structure according to claim 7, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.
9. The X-ray mask structure according to claim 7, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.
10. The X-ray mask structure according to claim 9, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.
11. The X-ray mask structure according to claim 9, wherein the X-ray absorber has an oxide film of a metal having an atomic number of 70 or more.
12. The X-ray mask structure according to claim 11, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

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13. An X-ray mask structure according to claim 1, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

14. An X-ray mask structure comprising:
an X-ray absorber having a masking pattern;
an alignment mark;
an X-ray permeable film for supporting the X-ray absorber and the mark on a surface of the X-ray permeable film;
a supporting frame for supporting the X-ray permeable film; and
a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon.

15. The X-ray mask structure according to claim 13, wherein the metal oxide film is formed on the portion of

X-ray permeable film having no alignment mark thereon.

16. The X-ray mask structure according to claim 14, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.

17. The X-ray mask structure according to claim 14, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.

18. The X-ray mask structure according to claim 17, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.

19. The X-ray mask structure according to claim 17, wherein the X-ray absorber comprises an oxide film of a metal having an atomic number of 70 or more.

20. The X-ray mask structure according to claim 19, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

21. The X-ray mask structure according to claim 14 further comprising an intermediate layer formed between the X-ray absorber and the X-ray permeable film, and between the alignment mark and the X-ray permeable film.

22. The X-ray mask structure according to claim 21, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.

23. The X-ray mask structure according to claim 21, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.

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24. The X-ray mask structure according to claim 23, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.

25. The X-ray mask structure according to claim 23, wherein the X-ray absorber comprises an oxide film of a metal having an atomic number of 70 or more.

26. The X-ray mask structure according to claim 25, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

27. The X-ray mask structure according to claim 14, wherein the alignment mark is formed on the metal oxide film.

28. An X-ray mask structure according to claim 14, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

29. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the surface of the X-ray permeable film having no X-ray absorber thereon.

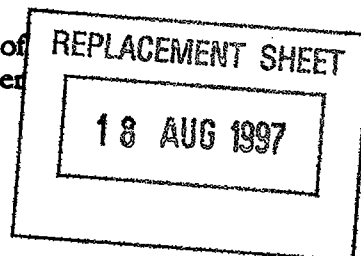
30. A semiconductor device according to claim 29, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

31. A method for manufacturing an X-ray mask structure comprising:

forming an X-ray absorber including a masking pattern, an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, and a supporting frame supporting the X-ray permeable film; and

thereafter subjecting a portion of the one surface of the X-ray permeable film having no X-ray absorber pattern thereon to an oxidation treatment.

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32. The method for manufacturing an X-ray mask structure according to claim 31, wherein the oxidation treatment is an oxygen plasma treatment.

33. The method for manufacturing an X-ray mask structure according to claim 31, wherein the oxidation treatment is an oxygen ion injection treatment.

34. The method for manufacturing an X-ray mask structure according to claim 31, wherein the oxidation treatment is a heat treatment in an oxygen atmosphere.

35. The method for manufacturing an X-ray mask structure according to claim 31, further comprising subjecting the surface of the X-ray absorber pattern to an oxidation treatment.

36. The method for manufacturing an X-ray mask structure according to claim 35, wherein the oxidation treatment is an oxygen plasma treatment.

37. The method for manufacturing an X-ray mask structure according to claim 35, wherein the oxidation treatment is an oxygen ion injection treatment.

38. The method for manufacturing an X-ray mask structure according to claim 35, wherein the oxidation treatment is a heat treatment in an oxygen atmosphere.

39. The method for manufacturing an X-ray mask structure according to claim 35, wherein the oxidation treatment of the X-ray permeable film and the oxidation treatment of the X-ray absorber are carried out in one process.

40. A method according to claim 31, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the subjecting step comprises subjecting a portion of the upper surface of the X-ray permeable film having no X-ray absorber pattern thereon to an oxidation treatment.

41. A method for manufacturing an X-ray mask structure comprising:

forming an X-ray absorber including a masking pattern, an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, and a supporting frame supporting the X-ray permeable film;

forming a metal film on the one surface of the X-ray permeable film;

forming an X-ray absorber pattern on the metal film;

and

thereafter, subjecting a portion of the one surface of the metal film having no X-ray absorber pattern thereon to an oxidation treatment.

42. The method for manufacturing an X-ray mask structure according to claim 41, wherein the oxidation treatment is an oxygen ion injection treatment.

43. The method for manufacturing an X-ray mask structure according to claim 41, wherein the oxidation treatment is a heat treatment in an oxygen atmosphere.

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44. The method for manufacturing an X-ray mask structure according to claim 41, further comprising subjecting the surface of the X-ray absorber pattern to an oxidation treatment.

45. The method for manufacturing an X-ray mask structure according to claim 44, wherein the oxidation treatment is an oxygen plasma treatment.

46. The method for manufacturing an X-ray mask structure according to claim 44, wherein the oxidation treatment is an oxygen ion injection treatment.

47. The method for manufacturing an X-ray mask structure according to claim 44, wherein the oxidation treatment is a heat treatment in an oxygen atmosphere.

48. The method for manufacturing an X-ray mask structure according to claim 44, wherein the oxidation treatment of the metal film on the X-ray permeable film and the oxidation treatment of the X-ray absorber are carried out in one process.

49. The method for manufacturing an X-ray mask structure according to claim 41, wherein said oxidation treatment step comprises producing an oxide film of the metal, in order to increase permeability of at least alignment light.

50. The method for manufacturing an X-ray mask structure according to claim 41, wherein the oxidation treatment is an oxygen plasma treatment.

51. A method according to claim 41, wherein (i) the X-ray-permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film, (iii) the metal film is formed on the upper surface of the X-ray permeable film and (iv) the subjecting step comprises subjecting a portion of the upper surface of the metal film having no X-ray absorber thereon to an oxidation treatment.

52. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an alignment mark, (iii) an X-ray permeable film supporting the X-ray absorber and the mark on a surface of the X-ray permeable film, (iv) a supporting frame supporting the X-ray permeable film and (v) a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon, to form a circuit pattern on the material to be exposed.

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53. A semiconductor device according to claim 52, wherein (i) the X-ray permeable film supports the X-ray absorber and the mark on the upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on at least the portion in the vicinity of the mark and having no X-ray absorber thereon.

54. An X-ray exposing method which comprises a step of irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an alignment mark, (iii) an X-ray permeable film supporting the X-ray absorber and the mark on a surface of the X-ray permeable film, (iv) a supporting frame supporting the X-ray permeable film and (v) a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon.

55. An X-ray exposing method according to claim 54, wherein (i) the X-ray permeable film supports the X-ray absorber and the mark on the upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on at least the portion in the vicinity of the mark and having no X-ray absorber thereon.

56. An X-ray exposing method which comprises a step of irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an alignment mark, (iii) an X-ray permeable film supporting the X-ray absorber and the mark on a surface of the X-ray permeable film, (iv) a supporting frame supporting the X-ray permeable film and (v) a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon, after alignment is carried out between the mask structure and the material to be exposed.

57. An X-ray exposing method according to claim 56, wherein (i) the X-ray permeable film supports the X-ray absorber and the mark on the upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on at least the portion in the vicinity of the mark and having no X-ray absorber thereon.

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58. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an alignment mark, (iii) an X-ray permeable film supporting the X-ray absorber and the mark on a surface of the X-ray permeable film, (iv) a supporting frame supporting the X-ray permeable film and (v) a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon, after alignment is carried out between the mask structure and the material to be exposed, thereby forming a circuit pattern on the material to be exposed.

59. A semiconductor device according to claim 58, wherein (i) the X-ray permeable film supports the X-ray absorber and the mark on the upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on at least the portion in the vicinity of the mark and having no X-ray absorber thereon.

60. An X-ray exposing method which comprises a step of irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon.

61. An X-ray exposing method according to claim 60, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

62. An X-ray exposing method which comprises a step of irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon, after alignment is carried out between the mask structure and the material to be exposed.

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63. An X-ray exposing method according to claim 62, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

64. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon, after alignment is carried out between the mask structure and the material to be exposed, thereby forming a circuit pattern on the material to be exposed.

65. A semiconductor device according to claim 64, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

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What is claimed is:

1. An X-ray mask structure comprising:
an X-ray absorber having a masking pattern;
an X-ray permeable film for supporting the X-ray absorber on one surface of the X-ray permeable film;
a supporting frame for supporting the X-ray permeable film; and
a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon.
2. The X-ray mask structure according to claim 1, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.
3. The X-ray mask structure according to claim 1, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.
4. The X-ray mask structure according to claim 3, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.
5. The X-ray mask structure according to claim 3, wherein the X-ray absorber has an oxide film of a metal having an atomic number of 70 or more.
6. The X-ray mask structure according to claim 5, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.
7. The X-ray mask structure according to claim 1, wherein an intermediate layer is formed between the X-ray permeable film and the X-ray absorber, and the metal oxide film is an oxide of a metal constituting the intermediate layer.
8. The X-ray mask structure according to claim 7, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.
9. The X-ray mask structure according to claim 7, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.
10. The X-ray mask structure according to claim 9, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.
11. The X-ray mask structure according to claim 9, wherein the X-ray absorber has an oxide film of a metal having an atomic number of 70 or more.
12. The X-ray mask structure according to claim 11, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.



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13. An X-ray mask structure according to claim 1, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

14. An X-ray mask structure comprising:
an X-ray absorber having a masking pattern;
an alignment mark;
an X-ray permeable film for supporting the X-ray absorber and the mark on a surface of the X-ray permeable film;
a supporting frame for supporting the X-ray permeable film; and
a metal oxide film formed on at least a portion of the surface of the X-ray permeable film in the vicinity of the mark and having no X-ray absorber thereon.

15. The X-ray mask structure according to claim 14, wherein the metal oxide film is formed on the portion of the X-ray permeable film having no alignment mark thereon.

16. The X-ray mask structure according to claim 14, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.

17. The X-ray mask structure according to claim 14, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.

18. The X-ray mask structure according to claim 17, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.

19. The X-ray mask structure according to claim 17, wherein the X-ray absorber comprises an oxide film of a metal having an atomic number of 70 or more.

20. The X-ray mask structure according to claim 19, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

21. The X-ray mask structure according to claim 14, further comprising an intermediate layer formed between the X-ray absorber and the X-ray permeable film, and between the alignment mark and the X-ray permeable film.

22. The X-ray mask structure according to claim 21, wherein the metal oxide film has a thickness of 8 Å to 1000 Å.

23. The X-ray mask structure according to claim 21, wherein the metal oxide film comprises an oxide of a metal having an atomic number of 35 or less.

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24. The X-ray mask structure according to claim 23, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.

25. The X-ray mask structure according to claim 23, wherein the X-ray absorber comprises an oxide film of a metal having an atomic number of 70 or more.

26. The X-ray mask structure according to claim 25, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

27. The X-ray mask structure according to claim 14, wherein the alignment mark is formed on the metal oxide film.

28. An X-ray mask structure according to claim 14, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

29. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon.

30. A semiconductor device according to claim 29, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon, to form a circuit pattern on the material to be exposed.

31. A method for manufacturing an X-ray mask structure comprising:

forming an X-ray absorber including a masking pattern, an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, and a supporting frame supporting the X-ray permeable film; and

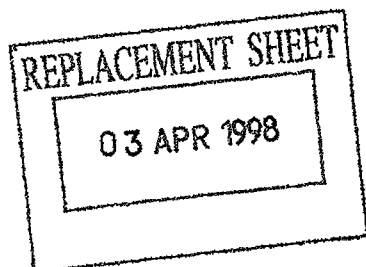
thereafter subjecting a portion of the one surface of the X-ray permeable film having no X-ray absorber pattern thereon to an oxidation treatment.



63. An X-ray exposing method according to claim 62, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

64. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon, after alignment is carried out between the mask structure and the material to be exposed, thereby forming a circuit pattern on the material to be exposed.

65. A semiconductor device according to claim 64, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.



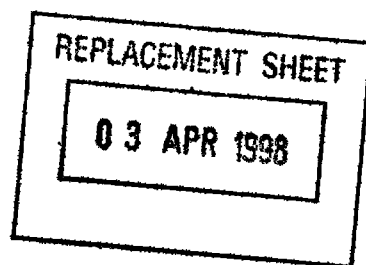
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**X-RAY MASK STRUCTURE AND X-RAY EXPOSING METHOD, AND
SEMICONDUCTOR DEVICE MANUFACTURED BY USE OF X-RAY MASK
STRUCTURE, AND METHOD FOR MANUFACTURING X-RAY MASK
STRUCTURE**

ABSTRACT OF THE DISCLOSURE

An X-ray mask structure comprises an X-ray absorber having a desired pattern, an X-ray permeable film supporting the X-ray absorber, and a supporting frame for supporting the X-ray permeable film. The X-ray mask structure has a metal oxide film formed on the portion of the X-ray permeable film having no X-ray absorber thereon.

Figure 1A



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24. The X-ray mask structure according to claim 23, wherein the metal is at least one selected from the group consisting of chromium, titanium, aluminum, zinc, copper and nickel.

25. The X-ray mask structure according to claim 23, wherein the X-ray absorber comprises an oxide film of a metal having an atomic number of 70 or more.

26. The X-ray mask structure according to claim 25, wherein the metal having an atomic number of 70 or more is at least one selected from the group consisting of tantalum, tungsten, platinum, gold and lead.

27. The X-ray mask structure according to claim 14, wherein the alignment mark is formed on the metal oxide film.

28. An X-ray mask structure according to claim 14, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

29. A semiconductor device manufactured by irradiating a material to be exposed with X-rays through an X-ray mask structure comprising (i) an X-ray absorber having a masking pattern, (ii) an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, (iii) a supporting frame supporting the X-ray permeable film and (iv) a metal oxide film formed on a portion of the one surface of the X-ray permeable film having no X-ray absorber thereon, to form a circuit pattern on the material to be exposed.

30. A semiconductor device according to claim 29, wherein (i) the X-ray permeable film supports the X-ray absorber on an upper surface of the X-ray permeable film, (ii) the supporting frame supports the X-ray permeable film from a lower surface of the X-ray permeable film and (iii) the metal oxide film is formed on the upper surface of the X-ray permeable film and on the portion having no X-ray absorber thereon.

31. A method for manufacturing an X-ray mask structure comprising:

forming an X-ray absorber including a masking pattern, an X-ray permeable film supporting the X-ray absorber on one surface of the X-ray permeable film, and a supporting frame supporting the X-ray permeable film; and

thereafter subjecting a portion of the one surface of the X-ray permeable film having no X-ray absorber pattern thereon to an oxidation treatment.

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