

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.

15

## 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  $\mu\text{m}$  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.

8  
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  $\mu\text{m}$  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  $\mu\text{m}$ ) having a thickness of about 0.75  $\mu\text{m}$

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.

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

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

20 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  $\mu\text{m}$ , more preferably 1 to 2  $\mu\text{m}$ .

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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 12 of silicon nitride  
having a thickness of 2  $\mu$ 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/cm<sup>2</sup> 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  $1 \times 10^{-5}$  Torr, and  
10 20 sccm of an argon gas was fed and 200 W was then  
applied under  $5 \times 10^{-2}$  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  $5 \times 10^{-2}$  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  $1 \times 10^{-6}$  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  $650^{\circ}\text{C}$  and a high-frequency power of 50 W  
was then applied under a pressure of  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 32 of silicon carbide  
having a thickness of 2  $\mu\text{m}$ .

Afterward, the film was set on a two-  
10 dimensional sputtering equipment, and after back  
pressure was reduced to  $2 \times 10^{-6}$  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  $10 \times 10^{-2}$  Torr to form a  
15 chromium film having a thickness of 200 Å 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 Å 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  $110^{\circ}\text{C}$   
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  $1 \times 10^{-5}$  Torr, 50 sccm of a  $CF_4$   
gas was fed and 200 W was then applied under  $5 \times 10^{-2}$   
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/cm<sup>2</sup> 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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 42 of silicon nitride  
5 having a thickness of 2  $\mu\text{m}$ .

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/cm<sup>2</sup> 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  $1 \times 10^{-5}$  Torr, and  
5   20 sccm of an argon gas was fed and 200 W was then  
applied under  $5 \times 10^{-2}$  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  $\mu\text{m}$  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/cm<sup>2</sup> 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/cm<sup>2</sup> 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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to form an X-ray permeable film 52 of silicon nitride having a thickness  
15 of 2  $\mu\text{m}$ .

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/cm<sup>2</sup> 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  $1 \times 10^{-5}$  Torr, and 20 sccm of an argon gas was fed  
and 200 W was then applied under  $5 \times 10^{-2}$  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  $5 \times 10^{-2}$  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  $\mu\text{m}$   
(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  $1 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
15 form an X-ray permeable film 72 of silicon carbide  
having a thickness of 2  $\mu$ m.

Afterward, the film was set on a two-  
dimensional sputtering equipment, and after back  
pressure was reduced to  $2 \times 10^{-6}$  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  $10 \times 10^{-2}$  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  $1 \times 10^{-5}$  Torr, 50 sccm of a  $\text{CF}_4$   
gas was fed and 200 W was then applied under  $5 \times 10^{-2}$   
Torr to etch W.

20 Since scarcely etched with the  $\text{CF}_4$  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  $\mu\text{m}$ . 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  $5 \times 10^{-2}$   
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 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 76' was measured again by means of the  
25 light wave interference system coordinate measuring  
equipment, it decreased to 0.05  $\mu\text{m}$ . 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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 82 of silicon nitride  
having a thickness of 2  $\mu$ 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  $2 \times 10^{-6}$  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  $10 \times 10^{-2}$  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  $1 \times 10^{-5}$  Torr, 50 sccm of a  $\text{CF}_4$   
gas was fed and 200 W was then applied under  $5 \times 10^{-2}$   
Torr to etch W. Since scarcely etched with the  $\text{CF}_4$  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  $\mu\text{m}$ . 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  $\mu\text{m}$ . 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  $\mu\text{m}$  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/cm<sup>2</sup> 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  $\mu\text{m}$ . 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/cm<sup>2</sup> 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  $\mu\text{m}$   
(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  $1 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 102 of silicon carbide  
having a thickness of 2  $\mu\text{m}$ .

5           Afterward, the film was set on a two-  
dimensional sputtering equipment, and after back  
pressure was reduced to  $2 \times 10^{-6}$  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  $10 \times 10^{-2}$  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  $1 \times 10^{-5}$  Torr, 50 sccm of a  $\text{CF}_4$   
gas was fed and 200 W was then applied under  $5 \times 10^{-2}$   
Torr to etch W. Since scarcely etched with the  $\text{CF}_4$  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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 112 of silicon nitride  
15 having a thickness of 2  $\mu$ 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/cm<sup>2</sup> 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 10<sup>16</sup>-10<sup>17</sup> ions/cm<sup>2</sup> 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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to form an X-ray  
permeable film 122 of silicon nitride having a  
thickness of 2  $\mu\text{m}$ .

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/cm<sup>2</sup> 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  $1 \times 10^{-5}$   
Torr, 20 sccm of an argon gas was fed thereto and 200 W  
10 was then applied under a pressure of  $5 \times 10^{-2}$  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  $5 \times 10^{-2}$  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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
form an X-ray permeable film 132 of silicon nitride  
15 having a thickness of 2  $\mu$ 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/cm<sup>2</sup> 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  $1 \times 10^{-5}$   
Torr, 20 sccm of an argon gas was fed thereto and 200 W  
was then applied under a pressure of  $5 \times 10^{-2}$  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  $5 \times 10^{-2}$  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  $\text{SiO}_2$  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  $2 \times 10^{-6}$  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  $5 \times 10^{-3}$  Torr to  
20 form an X-ray permeable film 142 of silicon nitride  
having a thickness of 2  $\mu\text{m}$ .

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/cm<sup>2</sup> 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  $1 \times 10^{-5}$   
Torr, 20 sccm of an argon gas was fed thereto and 200 W  
20 was then applied under a pressure of  $5 \times 10^{-2}$  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  $\text{SiO}_2$  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  $\mu\text{m}$  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/cm<sup>2</sup> 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/cm<sup>2</sup> 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.

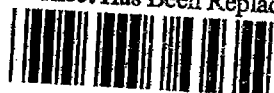
20

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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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.

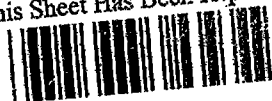
24. The X-ray mask structure according to  
10 Claim 23 wherein the metal is at least one selected  
from the group consisting of chromium, titanium,  
aluminum, zinc, copper and nickel.

25. The X-ray mask structure according to  
15 Claim 23 wherein the X-ray absorber has 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. An X-ray exposing method which comprises  
25 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.

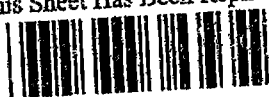
34. The method for manufacturing an X-ray mask  
structure according to Claim 31 wherein the oxidation  
15 treatment is a heat treatment in an oxygen atmosphere.

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.

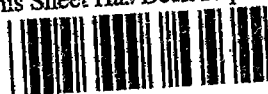
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