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S P E C I F I C A T I O N

15

TO ALL THOM IT MAY CONCERN:

Be it known that we, NOBUO KUSHIBIKI,
HIDEO KATO, AKIRA MIYAKE and YASUAKI FUKUDA, subject
of Japan, respectively at 2-2, Fukuda 5-chome, Yamato-shi,
20 Kanagawa-ken, Japan, 1678-10, Ichigao-cho, Midori-ku,
Yokohama-shi, Kanagawa-ken, Japan, Canon Honatsugi-ryo,
6-29, Mizuhiki 2-chome, Atsugi-shi, Kanagawa-ken, Japan
and 493-7-4-305, Tsurumaki, Hatano-shi, Kanagawa-ken,
Japan, have jointly invented a certain new and useful
25 improvement in X-RAY MASK SUPPORT AND PROCESS FOR
PREPARATION THEREOF of which the following is a full,
clear concise and exact description.

1 TITLE OF THE INVENTION

X-ray Mask Support And Process For Preparation
Thereof

5 BACKGROUND OF THE INVENTION

Field of The Invention

The present invention relates to a support for
a mask used in X-ray lithography processing for
preparing integrated circuits, and a process for
10 preparing the support.

Related Background Art

Recent semiconductor integrated circuits are
demanded to be made small in size and made highly
integrated, and a method of forming finer patterns is
15 required in the preparation process therefor.

Accordingly, it has become popular to utilize the
techniques of X-ray lithography.

In general, a mask used in the X-ray
lithography processing comprises a support frame
20 having the shape of a ring or the like and a film
member having X-ray transmitting portions and X-ray
non-transmitting portions. The film member covers the
opening of the support frame. In usual cases, the X-
ray non-transmitting portions are formed of a X-ray
25 opaque or absorbing material having a geometrical
pattern and provided on a mask support film (membrane)

1 that constitute a base for the film member, and the X-ray transmitting portions are formed of the mask support film itself corresponding to the part on which the X-ray opaque or absorbing material is not
5 provided.

The X-ray opaque or absorbing material must be formed on the mask support film with a submicroscopic size, with a good precision and with good reproducibility, and also the mask support film
10 is required to have dimensional stability. The mask support film, which covers the support frame with a considerable tension, is also required to have mechanical strength.

Since it is required to transfer mask patterns
15 to a semiconductor wafer with a submicroscopic size and precision without causing any deformation even by the heat due to the absorption of the incidence of X-rays, a mask support film comprising a ceramic material has been proposed so that the above
20 requirements can be fulfilled.

The support film comprising a ceramic material is prepared by forming a film on a substrate by a gaseous phase method such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and molecular
25 beam deposition (MB), followed by removal of the substrate.

1 Preparation of the mask support film
comprising SiC, which is a preferred ceramic in view
of the mechanical strength or less thermal
deformation, is carried out according to a gaseous
5 phase film deposition method typified by the method
described in Japanese Patent Publication No. 53-24785,
in which reactive ion-plating method is employed to
produce an SiC film on a silicon substrate in an
atmosphere of a hydrocarbon having 1 or 2 carbon
10 atoms.

However, such a preparation method according
to the gaseous phase film deposition has a difficulty
in mass production, resulting in expensiveness,
because a gaseous phase film deposition apparatus is
15 very expensive, the number of the films that can be
formed at one time is limited, and the film deposition
rate which is not high. Besides, it has been not
suitable to the mass production also from the
following reasons:

20 (a) Since the properties of films to be formed
depends on various parameters such as substrate
temperature, gas concentration and gas purity which
are entangled with each other, conditions for film
deposition must be set with complicity and also can be
25 maintained with difficulty.

(b) The operation to remove the substrate by

1 etching or the like after film deposition is
essential, and such an operation is cumbersome.

There is also the problem that a film having
irregularities of the same as an order of its
5 thickness is formed because, in the mask support film
formed by the gaseous phase film deposition method,
crystals that grow from various points on the
substrate collide with each other and the axis or
lattice plane of crystal appear almost randomly.

10 The irregularities on the surface of the
support film bring about the following undesirable
results.

(1) Because of the crystal particle diameter that
comes to be from $\sim 1 \mu\text{m}$ to several μm , the visible
15 light or near infrared light used for alignment
undergoes so large scattering that the transmittance
may be lowered and the S/N ratio of the alignment
light signal may be lowered.

(2) Since the irregularities indicate a thickness
20 non-uniformity, they may cause non-uniformity in the
intensity of transmitting X-rays.

(3) Because of unsmoothness of the surface, there
may be caused deterioration of precision, non-
uniformity in the thickness of X-ray opaque or
25 absorbing materials, and adhesion failure of X-ray
opaque or absorbing material patterns, when fine

1 patterns are formed.

Moreover, the film is so thin and so hard that it can be flattened with difficulty. Thus, the mask support film having surface roughness is not suitable
5 to the formation of X-ray opaque or absorbing materials with good precision, and the mask support film formed by the gaseous phase method have not necessarily had satisfactory performances. In addition, an adhesive is always used to fix the above
10 ceramic film to a support member, but adhesives for practical use are organic polymers. Accordingly, even when a heat-resistant adhesive such as polyimide is used, the tension applied to the film is loosened to make it difficult to retain the submicron patterns,
15 because of the large thermal expansion coefficient (about 100 times the ceramics) of such heat-resistant adhesive.

SUMMARY OF THE INVENTION

20 The present invention has been made to solve such problems, and a principal object thereof is to provide an X-ray mask support film having good performances, that can suppress strains produced by irradiation with X-rays to zero or to a level as
25 minimum as possible, may not cause the lowering of S/N ratio of the alignment light signal, and may not cause

1 not only the non-uniformity in the intensity of
transmitting X-rays or non-uniformity in the thickness
of X-ray opaque or absorbing material but also the
adhesion failure of the X-ray opaque or absorbing
5 material patterns.

The present invention provides an X-ray mask
support comprising a support frame and a support film,
wherein the support frame and support film have both a
thermal expansion coefficient of not more than
10 $1 \times 10^{-5} \text{K}^{-1}$.

In another embodiment, the present invention
provides an X-ray mask support comprising a support
frame and a support film, wherein the thermal
expansion coefficient of said support film does not
15 exceed the thermal expansion coefficient of said
support frame.

In still another embodiment, the present
invention provides an X-ray mask support comprising a
support frame and a support film, wherein said support
20 frame and said support film have both a thermal
expansion coefficient of not more than $1 \times 10^{-5} \text{K}^{-1}$ and
said support film has a surface roughness at least on
the mask surface, of not more than 10 nm r.m.s.

The present invention also provides a process
25 for preparing an X-ray mask support film, comprising
the steps of forming a film on a substrate, and

1 sintering said film.

In a further embodiment of the process, the present invention provides a process for preparing an X-ray mask support film, comprising the steps of
5 forming a film on a substrate comprising a compound having the same constituent as that of a sintered product of said film, and sintering said film.

Other embodiments of the process will become apparent from the following description.

10

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 and Fig. 2 are a view illustrating an integrally formed body comprising a support frame and a support film;

15 Fig. 3 to Fig. 5 are cross sectional views exemplifying various embodiments of light-irradiation methods in the present invention;

Fig. 6 is a view illustrating structures of a support frame and a support film which have the same
20 form as each other and are fixed through an adhesive layer; and

Fig. 7 is a view illustrating a process in Example 4.

25 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The X-ray mask support film of the present

1 invention comprises a support frame and a support
film, and is characterized in that both of the support
frame and support film comprise a material having a
thermal expansion coefficient of not more than
5 $1 \times 10^{-5} \text{K}^{-1}$ or a material such that the thermal
expansion coefficient of said support film does not
exceed the thermal expansion coefficient of said
support frame.

The present invention will be described below
10 in detail.

In the present invention, the material that
has a thermal expansion coefficient of not more than
 $1 \times 10^{-5} \text{K}^{-1}$ and a Young's modulus of not less than 10
GPa may typically include ceramics. They include, for
15 example, ceramics such as silicon nitride, silicon
carbide, sialon (Si, Al, O, N) in which part of
silicon of silicon nitride has been substituted with
aluminum and part of nitrogen thereof has been
substituted with oxygen, and carbon or graphite. Of
20 the above materials, particularly preferably used in
the present invention are silicon nitride and silicon
carbide.

The feature that the thermal expansion
coefficient is not more than $1 \times 10^{-5} \text{K}^{-1}$ requires
25 that, assuming a mask pattern on a support member to

1 be 1 cm, the elongation caused by a temperature change
of 1°C is not more than 10^{-7} . To retain the submicron
patterns, the thermal expansion coefficient must be
not more than $1 \times 10^{-5} \text{K}^{-1}$.

5 The feature that the thermal expansion
coefficient of the support film is smaller than that
of the support frame is advantageous for retaining the
state that the film is stretched, since the frame
undergoes a larger thermal expansion than the film
10 when exposed to heat.

 The above ceramics have differences in
particle diameter, particle size distribution, or
crystal form including three types of a cubic system
(β), a hexagonal system (α) and amorphous in case of
15 Silicon carbide, and also three types of a hexagonal
system (α), trigonal (β) and amorphous in case of
Silicon nitride. These structural differences result in
differences in values of physical properties, based on
differences in preparation methods. Accordingly, the
20 thermal expansion coefficient of the support frame can
be readily set so as not to exceed that of the support
film.

 In the case of carbon or graphite, when it is
obtained by sintering a pitch, the above setting can
25 be easily carried out by controlling the degree of
graphite formation and the layer structure.

1 The film is subjected to a constant stress to maintain the flatness, where its elongation must be very small, and hence the film is required to be stretched with a tension of from 10 to 100 MPa.

5 What is required in the submicron processing is to withstand the stress to give no elongation, and this is preferred for the reason that the dimensional precision can be retained. It is also preferred for the support film to have a thermal conductivity of not
10 less than $4 \text{ W/m}\cdot\text{K}$, for the reason that the local distortion produced by the temperature rise caused by irradiation with X-rays can be suppressed owing to heat conduction.

In the present invention, an organosilicon
15 polymer may be used. The organosilicon polymer
includes, for one example, a polymer generically
termed as polysilane represented by the general
formula:



wherein R' is methyl; R" is methyl, ethyl, cyclohexyl, phenyl, phenetyl, or tolyl; and n is not less than 100, more preferably not less than 200.

It may specifically include

1 poly(dimethylsilane-methylphenylsilane),
poly((dimethylsilane-methylcyclohexylsilane) and
poly(methylphenethylsilane-methylphenethylsilane).
Readily available is poly(dimethylsilane-
5 methylphenylsilane).

Another example of the organosilicon polymer
is a polymer generically termed as polysilazane
represented by the general formula:



wherein R is hydrogen, C₁ to C₈ alkyl, or aryl
such as phenyl, benzyl or phenethyl, n is not
less than 100, preferably not less than 200.

15 It specifically includes poly(methylsilazane),
poly(ethylsilazane) and poly(phenylsilazane).

In the case of carbon, petroleum pitch
commonly used in formation of carbon fiber may be
molded according to a molding method such as press
20 molding, injection molding or cast molding in a mold
previously prepared, since it has melt properties
similar to organic polymers.

Of the materials described above, preferably
used in the present invention are particularly
25 polysilane and polysilazane. Employment of these
materials as described above and the preparation

1 method as described below makes it possible to well
satisfy the preferable conditions as required herein.

Hitherto well known methods of preparing
silicon carbide include a method in which silica is
5 carbonized by reduction using carbon, and a method in
which metal silicon, silicon monoxide or silicon
dioxide is reacted with carbon. In the case of
silicon nitride, known are methods in which are direct-
nitriding of metal silicon, silica reduction, a imide
10 nitride thermal decomposition, etc.

The above polymers have recently been founded,
which are polymers for use in silicon carbide or
silicon nitride, comprising silicon as a polymer
backbone and called ceramics precursor polymers to
15 which usual molding methods for thermoplastic resins
can be applied, and have been used in preparation of
ceramics. Also, in the case of carbon, carbon
materials synthesized from petroleum pitch have become
available on the market.

20 Typical processes for preparing the mask
support frame of the present invention include the
following (1), (2) and (3).

Process (1)

Polysilane, polysilazane or petroleum pitch-is
25 molded by a usual thermoplastic resin molding method
(such as compression or injection) at temperatures

1 higher than its melting point, using a mold capable of
integrally molding the support frame and support film
(Fig. 1).

It is preferred to bring a molded product to
5 have no edge as shown in Fig. 2, thereby making it
possible to effect mold release with ease.

Next, the resulting molded product is sintered
in an inert gas atmosphere to make an X-ray mask
support. Typical conditions for the sintering are as
10 follows: In the instance where the material comprises
polysilane, the sintering may be carried out at
temperatures raised up to 1,400°C in one stage, or
preferably used is the two-stage sintering such that
the sintering is carried out at 400 to 600°C for a
15 given time and thereafter the temperature is raised to
carry out the sintering at 1,100 to 1,400°C for a
given time.

In the instance where the material comprises
polysilazane, the sintering may be carried out
20 according to the two-stage sintering such that the
temperature is raised up to 500°C, which is maintained
for several to several ten hours, and then raised to
1,000°C.

Such sintering brings polysilane finally into
25 an SiC sinter from SiC-SiH₂; and petroleum pitch is
brought into graphite.

1 Even if no complete SiC formation, SiN
formation or carbon formation is effected, in other
words, even if SiC-SiH₂ or the like remains, the
previously described properties, required to the X-ray
5 mask support film of the present invention, can be
sufficiently exhibited.

Process (2)

The support frame alone is first prepared by
molding and sintering. There can be utilized known methods
of sinter-molding of SiC, SiN or carbon. Methods of
preparing silicon carbide include a method on which silica is
carbonized by reduction using carbon, and a method in which
metal silicon, silicon monoxide or silicon nitride is
reacted with carbon. In case of silicon nitride, methods
are known such as direct-nitriding of metal silicon, reduction
of silica, and thermal decomposition of imide nitride. In case
of carbon, a method is known in which e.g., petroleum pitch
is formed into graphite by sintering.

Next, a thin film (support film) comprising
the organosilicon polymer is formed on a substrate.
For that purpose, for example, the organosilicon
20 polymer may be dissolved in a solvent, and the
resulting solution may be coated on the substrate by
use of a coating method such as dipping, casting or
spin coating, optionally followed by drying.

The solvent to dissolve the organosilicon
25 polymer may typically include aromatic hydrocarbons
such as benzene and toluene, saturated hydrocarbons

1 such as benzene and toluene, saturated hydrocarbons
such as hexane and octane, halogen derivatives, and
cyclic ethers such as tetrahydrofuran.

Suitable values of concentration of the
5 organosilicon polymer solution used for the purpose of
coating the polymer may vary depending on the
conditions for film formation, but may be selected
from the range of from 3 % by weight to 60 % by
weight.

10 In forming the thin film on the substrate,
employment of the solution used as described above may
be replaced with employment of a melt of the
organosilicon polymer or the like.

More specifically, the organosilicon polymer
15 can be synthesized usually so as to have a molecular
weight of from several thousand to about 1,000,000,
and its melting point falls within the range of from
70 to 200°C depending on its average molecular weight.
Accordingly, the above film formation can be carried
20 out by melting the organosilicon polymer (for example,
at a temperature several ten degrees higher than its
melting point), followed by a commonly available
polymer film formation method such as pressing,
laminating or T-die extrusion.

25 In the case of carbon, the same method as in
the case of the polymer may be employed to form a film
on a suitable substrate by dissolving pitch in a

1 suitable diluent as exemplified by quinoline so that
the viscosity of pitch may fall within the range of
from 10 to 10,000 cP, or heating the pitch.

In any film formation method of the above, the
5 thin film formation is required to be made so that the
thin film formed may have a uniform thickness over the
whole.

On the thin film formed in the above manner
and comprising the organosilicon polymer or pitch, a
10 support frame previously prepared may be placed, and
they may be sintered under the conditions as explained
below, so that an X-ray support having sufficiently
satisfied the properties previously mentioned can be
obtained. The support film may preferably have a film
15 thickness of from 1 to 5 μm , particularly preferably
from 2 to 4 μm , in view of strength and X-ray
transmission.

In the above thin film comprising the
organosilicon polymer or pitch, a known sintering aid
20 may also be added in a trace amount (not more than 2
or 3 %). The sintering aid includes, for example,
 Al_2O_3 , BN and BeO.

In the above film of the organosilicon polymer
or pitch, fibers and/or fine particles of ceramics or
25 carbon may be contained, thereby making it easy to
make crystal control since the fibers or fine

1 particles serve as crystal nuclei at the time of the
sintering, so that a film having much better tensile
strength or impact strength can be obtained and the
sintering time can also be shortened. Further, in
5 view of the X-ray transmitting properties of the
support film, it is preferred that ceramics are used.

Regarding the ceramics used in the above
embodiment, there may be used ceramics whose main
component unit comprises silicon carbide in the
10 instance where a silicon carbide polymer such as
polysilane is used as the organosilicon polymer, and
may be used ceramics whose main component unit
comprises silicon nitride in the instance where a
silicon nitride polymer such as polysilazane is used.
15 Alternatively, there may be used sialon in which part
of silicon in silicon nitride has been substituted
with aluminum. An additive may also be added to these
ceramics. Such an additive may include, for example,
a sintering aid, boron nitride, alumina and yttrium
20 oxide.

As to the size of the ceramics, the fineness
of the ceramic fibers and particle diameter of the
ceramic fine particles may preferably be 3 μm or less
since the preferred thickness of the X-ray support -
25 film is 3 μm or less. Further, the fineness of the
ceramic fibers may more preferably be in the range of

1 from 0.05 to 1.5 μm . With regard to the particle
diameter of the ceramic fine particles, there is no
particular limitation in the lower limit for a
preferred range so long as it is not more than 0.3 μm .

5 The particle size distribution thereof may also be
broad without any disadvantage.

Formed is a film containing the above
described organosilicon polymer and ceramics in a
suitable proportion. The proportion may be selected
10 to find a suitable value depending on the type and
molecular weight of the silicon polymer and on, when a
solvent is mixed in the polymer, the type of the
solvent, the type of ceramics, and so forth.

There is no limitation in the film formation
15 method so long as the film can be formed to have a
desired structure so that the film having been
subjected to sintering may exhibit good properties as
the X-ray mask support film, but usable is, for
example, a method comprising laying up the ceramic
20 fibers and/or fine particles on a substrate,
impregnating the resulting layup with the
organosilicon polymer to have desired composition, and
forming the layup into a film.

Methods for the laying-up may include, for -
25 example, a method in which the ceramic fibers and/or
fine particles are laid up by allowing them to fall in

1 the air, a method in which they are laid up by
allowing them to settle in a liquid, a method in which
they are allowed to float in a liquid and a layup
layer is obtained by a papermaking method, and a
5 method in which a ceramic nonwoven fabric or woven
fabric is merely used as the above layup. Also, the
laying-up may preferably be carried out by wetting the
ceramic fibers and/or fine particles with a low-
melting organic solvent, thereby preventing them from
10 being electrically charged, so that the layup can be
obtained in a good state.

Methods of impregnating the layup obtained
according to such methods with the organosilicon
polymer may include a method in which the layup is
15 merely impregnated with a solution or melt of the
above organosilicon polymer, and a method in which the
surface of the layup is covered with solid powder of
the organosilicon polymer and then the surface is
pressed and heated, thus impregnating the former with
20 the latter.

Also, part of the above thin film of the
organosilicon polymer may be previously formed of a
silicon carbide material, so that the X-ray mask
support film comprising a silicon carbide film having
25 a surface roughness of 10 nm r.m.s. or less.

More specifically, a silicon carbide is first

1 formed into a film on a substrate typified by a
silicon wafer. For this purpose, a CVD process can be
utilized, for example. In this instance, SiH_4 and CH_4
are used as raw material gases, and the substrate is
5 heated to temperatures of from about 600 to 800°C.
The CVD process carried out under such conditions
brings about polycrystalline silicon carbide, thus
obtaining a film having a high modulus of elasticity.
The film thickness may desirably be selected so as to
10 be from about 1 to 3 μm so that X-rays can be
sufficiently transmitted.

The silicon carbide film thus formed has a
surface roughness of about 0.5 μm .

The substrate having the above SiC film may be
15 prepared not only by the CVD process but also by other
processes such as gaseous phase formation or sintering
of fine particles.

On the silicon carbide film formed on the
substrate according to the above method, the thin film
20 comprising the organosilicon polymer may be formed
according to the method previously described, so that
the organosilicon polymer film whose part has been
formed of silicon carbide or silicon nitride can be
formed on the substrate.

25 Here, in case of there is no particular
limitation in materials for the substrate used in the

1 present invention, and substrates made of various
materials can be used, so long as the substrate can
meet the conditions such that, when it is a substrate
to be removed before the sintering step as described
5 below and when the substrate peeling method as
described below is employed as the method for removing
it, it exhibits a peel readiness in such a degree that
the substrate and the film can be separated in a good
state, and, when a solvent is mixed in the
10 organosilicon polymer at the time of coating, it has
sufficient solvent resistance to that solvent.

Usable methods of peeling from a substrate the
film formed on the substrate include a method in which
it is mechanically peeled, a method in which it is
15 mechanically peeled by sticking a pressure-sensitive
adhesive, a bonding adhesive or the like, a method in
which it is peeled by immersing it in a solvent
insoluble or poorly soluble to the organosilicon
polymer, as exemplified by water and alcohol, and a
20 method in which the substrate is removed by
dissolution when the substrate is soluble to a solvent
that may not act on the organosilicon polymer.

Examples of the method in which the substrate is
removed by dissolution include a method in which a PVA
25 film or an NaCl sheet is used as the substrate and the
substrate is removed by dissolution using water, etc.,

1 and a method in which a polymethyl methacrylate sheet
is used as the substrate and is similarly removed by
dissolution using acetone or the like.

The organosilicon polymer of the present
5 invention is known to undergo cross-linking when
irradiated with light having a wavelength shorter than
350 nm (Lactualite Chimique, page 64, 1986, R. West).
Accordingly, in instances in which light-irradiation
is effected upon forming the film of the organosilicon
10 polymer, there may be conducted the irradiation with
light having a wavelength region corresponding
thereto, or light having a wavelength region of at
least from 300 to 350 nm. Specifically, it is
possible to use a high-pressure mercury lamp, an ultra-
15 high-pressure mercury lamp, a xenon lamp, etc. The
radiation heat that generates at the time of the above
light-irradiation in the present invention may not
particularly be removed.

In instances in which the sintering described
20 below is applied to a film brought to have its own
form without the use of a substrate as in the present
invention or, at the time of peeling, the peeling can
not be well carried out because of lack in the
strength of the film, a preferred method is to improve
25 the film strength by applying light-irradiation and
thereafter carry out the peeling. Embodiments of

1 typical methods for the light-irradiation for that
purpose will be described below with reference to the
drawings.

Fig. 3 is a cross-section illustrating an
5 embodiment of the light-irradiation methods in the
present invention. This embodiment is concerned with
a method in which uniform light-irradiation is applied
to the whole surface of an organosilicon polymer 1
from the upper part of the polymer laminated or coated
10 on a substrate 2. Employment of this embodiment makes
it possible to use as the substrate, various
substrates such as light-reflective substrate, light-
transmissive substrate and light-absorptive substrate
so long as they have sufficient peel readiness and
15 solvent resistance as previously mentioned.

Fig. 4 is a cross section illustrating another
embodiment of the light-irradiation in the present
invention. Used as the substrate in this embodiment
is a light-transmissive substrate 2a that does not
20 absorb light having wavelengths shorter than 350 nm,
and simultaneous irradiation of light on both the
surfaces of the organosilicon polymer 1 enables more
uniform cross-linking of the whole of the polymer 1.
The light-transmissive substrate 2a used in this
25 embodiment may specifically include glass having no
absorption band at a wavelength region of 290 nm or

1 more.

Fig. 5 is a cross section illustrating still another embodiment of the light-irradiation in the present invention. This embodiment is concerned with
5 a method in which two sheets of the above light-transmissive substrate 2a are used and the organosilicon polymer 1 is held between them and light-irradiation is effected from both surfaces thereof. Employment of this embodiment makes it able to prevent
10 surface irregularities owing to the evaporation of the solvent contained in the polymer 1 to form a smoother film.

In the present invention, the substrate that can be used when the substrate and film are sintered
15 together may be satisfactory if it is a heat-resistant substrate that can endure the sintering up to the stage at which the organosilicon polymer has cured by sintering and its flatness has come substantially not to be lost. Accordingly, it is also possible to use
20 as the heat-resistant substrate those which may disappear in the course of the sintering.

However, it is preferred that the heat-resistant substrate may not disappear or deform, from the viewpoint of the flatness of the X-ray mask
25 support film formed thereon, etc. Such a heat-resistant substrate may be satisfactory if it

1 comprises a material stable to a high temperature of
at at least 1,400°C, preferably 1,500°C or more. It
may specifically include ceramics as exemplified by
alumina and magnesium oxide, and graphite.

5 In instances in which materials like metal
silicon are utilized as the substrate, the substrate
can be removed from the support film by ion etching in
a gaseous phase, or by dissolution using acid or
alkali after sintering.

10 On the other hand, the heat-resistant
substrate that disappears in the course of the
sintering may include substrates made of a resin or
metal having thermal resistance up to about 300 to
400°C. Such disappearance of the heat-resistant
15 substrate results from decomposition, melting, etc.
occurring at 500 to 600°C.

As the above resin, suitably usable are the so-
called engineering plastics as exemplified by
polyoxymethylene, polyethersulfon, polyether ether
20 ketone and polybutylene terephthalate, and as the
metal, suitably usable are tin, lead, zinc and
aluminum.

It is also preferred from the viewpoint of the
surface smoothness of the resulting support film that
25 the root-mean-square roughness of the heat-resistant
substrate has a precision of not more than 10 nm.

1 Preparing the support film by using the above
substrate makes it possible to obtain an X-ray mask
support film having a surface roughness of not more
than 10 nm r.m.s.

5 The surface roughness at this time may
preferably be measured by a measurement method that
employs a non-contact optical roughness meter and can
measure the roughness without giving any stress at the
time of measurement, and it may be measured, for
10 example, with a digital optical linear profiler TOPO™-
2D (Wyko Corporation).

 The surface roughness as defined in the
present invention can be conveniently measured using
the above surface roughness meter.

15 The sintering step in the process of the
present invention comprises, when the film is prepared
according to the film formation method using a
solution and when polysilane is employed as the
organosilicon polymer, heating first the film for a
20 given time, raising the temperature to from 500 to
600°C, maintaining this temperature for a given time,
thereafter further raising the temperature to from
1,100 to 1,400°C, and maintaining this temperature for
a given time or gradually raising the temperature from
25 1,100°C up to about 1,400°C, thus making a film having
SiC crystals in a sintered state.

1 When polysilazan is employed as the
organosilicon polymer, the step comprises raising
first the temperature to 500°C, and thereafter raising
it to from 1,000 to 1,200 °C to carry out two-stage
5 sintering, or gradually raising the temperature from
1,000 to about 1,400 °C.

Typical examples for the heating rate or
heating retention time in the sintering are set out
later in Examples, but sintering conditions may be
10 appropriately selected so that the Young's modulus and
thermal expansion coefficient previously described may
be set at the intended values.

The sintering is carried out in an atmosphere
of inert gas, but the sintering may be carried out
15 using gases other than it if such sintering is carried
out at the stage in which the formation of SiC as the
X-ray mask support film may not substantially be
hindered.

Process (3)

20 Prepared first are structures of a support
frame and a support film each having the same form.
The structures may comprise sintered products made of
SiC, SiN or carbon, or products obtained by sintering
the organosilicon polymer at about several 100°C, or
25 molded products having plasticity. The sintered
products or the like can be prepared by employing the

1 same methods as described in Processes (1) and (2).

Next, on the structures of the support frame and support film each having the same form, a solution of the organosilicon polymer used in Process (2) is
5 coated or a melt of the organosilicon polymer heated to a temperature higher than the melting point is coated, and thereafter both structures (i.e., a support frame structure 4 and a support film structure
10 adhesive layer 3 comprising the organosilicon polymer or the like. To increase the adhesive force, a rougher adhering surface is preferred. Thereafter, sintering is carried out in the same manner as in Process (1), thus making an X-ray mask support.

15 For the solution or melt for use in provisionally adhering the above both structures, it is necessary to use the one that may form by sintering a sintered product having substantially the same composition as that of either of the support frame or
20 support film.

The X-ray mask support prepared in the above manner can be made free from the very cumbersome operation of particularly applying a stress to the support film to fix it uniformly, because a stress is
25 necessarily applied to the support film owing to the contraction that takes place on sintering. This also

1 makes it ready to prepare a homogeneous support film.

As described above, since no gaseous phase film formation may not be utilized in the present invention, preparation conditions can be set
5 relatively with ease, and mass production becomes possible. Also, since a high yield can be achieved, X-ray mask support films can be prepared at a low cost. It also has become possible to provide X-ray mask supports that may cause substantially no elongation of
10 adhesives, deformation of frame members and sag or distortion of support films even by heat generated by X-ray irradiation or the like, and also can have a high mechanical strength.

Moreover, since the surface of the support
15 film is so flat that preparing X-ray masks by using the same can bring about the effect such that;
(1) scattering of the visible light or infrared light for making alignment is small with high transmittance, resulting in improvement of the S/N ratio of the
20 alignment light signal;
(2) non-uniformity in the strength of transmitting X-rays becomes very small; and
(3) precision in forming fine patterns and adhesion of the X-ray opaque or absorbing material -
25 are improved, resulting in almost no non-uniformity in thickness of the X-ray opaque or absorbing material.

1 The present invention will be described below
in greater detail by giving specific Examples.

Example 1

Polysilastyrene (trade name: S-400, available
5 from NIPPON SODA CO., LTD.) was dissolved in
toluene to prepare a 10 wt/v% solution. A surface-
polished Al_2O_3 substrate having a surface roughness of
9 nm r.m.s. was set on a spinner (Mikasa Spinner 1H-2)
and rotated at 400 rpm, on which the above solution
10 was dropped, thus preparing a film of 31 μm thick.

Next, this film was placed in a sintering
furnace together with the substrate, and, under dry
nitrogen, heated at 200°C for 1 hour and further
raised up to 1,200°C at a rate of 10°C/min. The
15 furnace was maintained at this temperature for 1 hour,
followed by cooling to obtain a silicon carbide film
having a thickness of 2.9 μm and a surface roughness
of 8 nm.

The silicon carbide film was cut into a strip
20 of 10 x 50 mm², and its Young's modulus measured using
a tensile tester was found to be 200 GPa. Thermal
expansion coefficient was $7 \times 10^{-6} K^{-1}$.

The above polysilastyrene solution was coated
by brushing on a silicon carbide support frame (having
25 the shape of a ring of 75 mm in inner diameter, 90 mm
in outer diameter and 5 mm in thickness) obtained by a

1 reactive sintering process, and the above silicon
carbide film was fixed thereon, followed by sintering
under the same conditions as above to obtain an X-ray
mask support.

5 Example 2

A silicon carbide support frame similar to the
one used in Example 1 was placed on a carbon
substrate, and a polysilastyrene solution in a
concentration of 10 wt/v% was flowed thereon, followed
10 by drying to form a polysilastyrene film.

This was sintered in the same manner as in
Example 1. As a result, there was obtained an X-ray
mask support comprising the support frame and a
silicon carbide film fixed on the support frame.

15 Example 3

Inside of a 1 liter autoclave made of glass
was replaced with dry nitrogen, and charged therein
was 0.4 g of KH (100 mmol; 3.9 mol % based on
 CH_3SiHNNH).

20 Tetrahydrofuran (300 mL) was dropwise added
with a syringe in flask having a three-way cock, and
the mixture was stirred to disperse KH. Next, using a
syringe filled with nitrogen, 15.271 g (0.258 mol) of
(CH_3SiHNNH)₃ was slowly added to the stirred KH slurry
25 over a period of 15 minutes. After stirring at room
temperature for 90 minutes, generation of gas stopped,

1 and a transparent and homogeneous solution remained.
Addition thereto of 2.28 g (16.1 mmol) of methyl
iodide immediately resulted in formation of a white
precipitate of KI. This reaction mixture was further
5 stirred for 30 minutes. Next, most of the THF
solution was removed under reduced pressure, and 80 ml
of hexane was added to the remaining white slurry.
The resulting mixture was subjected to centrifugal
separation to separate supernatant liquid from a white
10 solid. This solution was subjected to a trap-to-trap
distillation, so that 15.1 g (99 % by weight) of a
white precipitate remained.

This was dissolved in toluene and spin-coated
on a carbon substrate having a surface roughness of 10
15 nm.

Placed thereon was a silicon nitride ring
having the same size as used in Example 1, which was
heated in a sintering furnace to 1,300°C, and
thereafter the furnace was maintained at this
20 temperature for 4 hours, followed by cooling to obtain
an X-ray mask support having a support film of 2.2 μm
in thickness and 9.5 nm in surface roughness.

Example 4

A mold 6 as shown in Fig. 7 was place on a -
25 heater, which was kept heated to 200°C, and a melt
flow indexer was connected to a hole provided on the

1 mold. Nozzle temperature was kept to 250°C, and
polysilastyrene was introduced. A weight (22.125 g)
was placed on the upper part and the polysilastyrene
was flowed in the mold until it flow out from another
5 hole. Thereafter, this was subjected to press molding
at 300°C under a pressure of 150 kg/cm². After
cooled, the molded product was heated to 600°C at a
rate of 5°C/min and kept at this temperature for 1
hour. Thereafter, after taken off from the mold, the
10 product was again heated to 1,350°C and kept at that
temperature for 1 hour followed by cooling. There was
obtained an integral type mask support comprising
silicon carbide.

Example 5

15 [X-ray mask support film (A)]

Polysilastyrene (trade name: S-400, available
from NIPPON SODA CO., LTD.) was dissolved in
toluene to prepare a 10 wt/v% solution. A surface-
polished carbon substrate (10 mm thick) having a
20 surface roughness of 7.5 nm when measured with the
surface roughness meter TOPO™-2D previously described
was set on a spinner (Mikasa Spinner 1H-2) and rotated
at 500 rpm, on which the above solution was dropped,
thus obtaining a film of 28 μm thick.

25 A carbon substrate polished similarly to the

1 above was laid overlapping, and the film was laminated
by pressing under a pressure of 10 kgf/cm^2 and at a
temperature of 180°C . In a sintering furnace whose
inside was replaced with dry nitrogen, the film was
5 heated at 200°C for 1 hour and then raised up to
 $1,350^\circ\text{C}$ at a rate of 10°C/min . The furnace was
maintained on this state for 1 hour, followed by
cooling.

The carbon substrate was taken off, and the
10 surface roughness of the film was measured, which was
found to be 9.0 nm . Film thickness was $2.6 \mu\text{m}$ and
thermal expansion coefficient was $5 \times 10^{-5} \text{ K}^{-1}$.

[X-ray mask support film (B)]

On a carbon substrate made ready for use in
15 the same manner as in the support film (A), a toluene
solution of 10 wt/v% polysilastyrene was spin-coated
with a spinner. Revolution number was set to 400 rpm,
and spin time to 30 seconds, thus obtaining a film of
 $3.2 \mu\text{m}$ thick. A carbon substrate finished similarly
20 to the above substrate was laid overlapping, and the
film was laminated in the same manner as in Example 1
by pressing under a pressure of 10 kgf/cm^2 and at a
temperature of 180°C . In a sintering furnace whose
inside was replaced with dry argon, the film was
25 heated at 500°C for 1 hour, and further raised up to
 $1,400^\circ\text{C}$ at a rate of 10°C/min . The furnace was

1 maintained on this state for 2 hours, and then left to cool.

The carbon substrate was taken off, and then the surface roughness of the film was measured, which
5 was found to be 8.0 nm. Film thickness was 2.9 μm and thermal expansion coefficient was $5 \times 10^{-5} \text{K}^{-1}$.

The film (A) and film (B) were adhered on a circular frame, made of e.g., stainless steel, having a larger thermal expansion coefficient (thermal
10 expansion coefficient: $2 \times 10^{-5} \text{K}^{-1}$) than that of the films of the above (A) and (B), while applying a tension. The film tension at this time was 70 MPa. On the film, an absorber (X-ray intercepting material) comprising gold was formed according to a usual mask
15 preparation process. As a result, the lowering of yield because of defects such as peeling-off of the absorber was remarkably suppressed as compared with an instance in which the absorber comprising gold was formed similarly on an SiC film formed according to
20 the CVD process commonly practiced and having a root-mean-square surface roughness of 50 nm. Also, the film was sagged upon X-ray irradiation in the case of a support in which a support frame (thermal expansion coefficient: $0.4 \times 10^{-6} \text{K}^{-1}$) made of quartz glass and
25 having a smaller thermal expansion coefficient was used in place of the above support frame.

1 For evaluation of performances, Young's
modulus of the above film was measured according to a
static pressure balloon method. As a result, there
was obtained a value of 200 GPa.

5 Example 6

Polysilastyrene (trade name: S-400, available
from NIPPON SODA CO., LTD.) was dissolved in
toluene to prepare a 10 wt/v% solution. A surface-
polished Al_2O_3 substrate having a surface roughness of
10 9 nm was set on a spinner (Mikasa Spinner 1H-2) and
rotated at 1,000 rpm, on which the above solution was
dropped, thus preparing a film of 31 μm thick.

Put thereon was a silicon carbide support
frame (having the shape of a ring of 75 mm in inner
15 diameter, 90 mm in outer diameter and 5 mm in
thickness) obtained according to a reactive sintering
process, and the film was heated in an atmosphere of
nitrogen at 200°C for 1 hour, and further raised up to
500°C at a rate of 10°C/min. The film was kept on
20 this state for 1 hour, and further heated up to
1,300°C at a rate of 5°C/min, which was maintained for
two hours, followed by cooling to obtain an X-ray mask
support having a silicon carbide film of 2.9 μm in
thickness and 8 nm in surface roughness.

25 Example 7

An X-ray mask support film comprising a

1 silicon carbide film was obtained in the same manner
as in Example 6 except that a polyether ether ketone
sheet was used as a substrate.

The resulting film showed the same properties
5 as in Example 6, and there was seen no difference
considered to be caused by the influence of the
decomposition of substrate polymer.

Example 8

[X-ray mask support film (C)]

10 On a silicon wafer (100) substrate of 0.5 mm
in thickness and 2.0 nm in surface roughness, an SiC
film was formed using a plasma CVD apparatus to have a
thickness of 2.0 μm . Used as raw material gases were
SiH₄ and CH₄, and the component ratio was kept at
15 1:10, pressure at 10 to 50 Torr, and substrate
temperature at 800°C. Thus, a film having a surface
roughness of 0.5 μm was obtained.

Next, this substrate was set on a spinner
(Mikasa Spinner 1H-2), and a solution obtained by
20 dissolving polysilastyrene (trade name: S-400,
available from NIPPON SODA CO., LTD.) in toluene
to give a concentration of 10 wt/v% was dropped on the
spinner which was rotated at 1,000 rpm, thus obtaining
a film of 7.2 μm thick.

25 Next, this film was placed in a sintering
furnace in which Ar gas is flowed, and temperature was

1 raised from room temperature up to 650°C at a rate of
10°C/hr, which was maintained for 40 hours.

Thereafter, the furnace was allowed to cool to room
temperature, and subsequently the temperature was

5 raised up to 1,000°C at a rate of 100°C/hr, which was
maintained for 30 hours. Thereafter, the furnace was
allowed to cool.

Finally, the Si wafer was anisotropically
etched from the back surface with use of an aqueous
10 KOH solution, and removed.

In this manner, there was obtained an X-ray
mask support film comprising a self-supporting SiC
film of 3.2 μm thick. This had a surface roughness of
2.0 nm on the surface that had been in contact with
15 the Si wafer and 8.0 nm on the opposite surface.

[X-ray mask support film (D)]

On a silicon wafer (100) substrate of 0.5 mm
in thickness, 76 mm in diameter and 2.0 nm in surface
roughness, an SiC film and a polysilastyrene film were
20 formed in the same manner as in support film (C).

They had a film thickness of 1.8 μm and 5.1 μm ,
respectively. The SiC film had a surface roughness of
11 nm. In a sintering furnace whose inside was
replaced with dry nitrogen, the product was sintered
25 at 700°C for 30 hours and at 1,050°C for 20 hours,
followed by slow cooling to room temperature.

1 Next, the silicon wafer was anisotropically
etched from the back surface with use of an aqueous
KOH solution, and removed. Thus, there was obtained
an X-ray mask support film.

5 The silicon carbide frame same as in Example 1
was provided on each of these films (C) and (D) in the
same manner as in Example 1 to obtain X-ray mask
supports. On each of these X-ray mask supports, an X-
ray absorber made of gold was formed according to a
10 usual mask preparation process. As a result, in each
film the defects such as peeling-off of the absorber
was remarkably decreased as compared with an instance
in which the absorber comprising gold was formed
similarly on an SiC film formed only according to the
15 CVD process commonly practiced and having a surface
roughness of 0.4 μm . Accordingly, the lowering of
yield was remarkably suppressed even when a large
number of X-ray masks were prepared. Also, the
transmittance of the visible light for alignment was
20 improved by 10 % or more.

Example 9

Polysilastyrene (trade name: S-400, available
from NIPPON SODA CO., LTD.) was dissolved in
toluene to prepare a 10 wt/v% solution. A surface-
25 polished Al_2O_3 substrate having a surface roughness of
9 nm was set on a spinner (Mikasa Spinner 1H-2) and

1 rotated at 400 rpm, on which the above solution was
dropped, thus preparing a film of 31 μm thick.

Subsequently, using a high-pressure mercury
lamp (USH-250), light irradiation was carried out on
5 the film for 20 minutes, which film was then immersed
in a mixed solvent of water:methanol = 1:1 for 1 hour
to peel the polysilastyrene film from the substrate.

Next, the resulting polysilastyrene film was
placed alone in a sintering furnace, and temperature
10 was raised from room temperature to 600°C at the rate
of 5°C/min. The furnace was maintained on this state
for 1 hour, and thereafter the temperature was raised
up to 1,300°C at the rate of 5°C/min. The furnace was
maintained on this state for 1 hour, followed by
15 cooling to obtain a silicon carbide film of 2.9 μm in
thickness and 8 nm in surface roughness.

The silicon carbide film was cut into a strip
of 10 x 50 mm², and its Young's modulus measured using
a tensile tester was found to be 200 GPa.

20 Example 10

A silicon carbide whisker (available from
Tateho Chemical Industries, Ltd.) of from 0.05 to 1.5
 μm in finess and from 5 to 200 μm in length was wetted
with ethanol, and laid up on a graphite sheet having a
25 surface roughness of 11 nm, followed by pressing under
a pressure of 10 kg/cm² to prepare a layup with a

1 thickness of 2 μm . Subsequently, ethanol in the layup
was evaporated, and the resulting layup was spray-
coated with a viscous solution obtained by dissolving
polysilastyrene (trade name: S-400, available from
5 NIPPON SODA CO., LTD.) in toluene to give a
concentration of 40 % by weight, followed by
evaporation of toluene.

Next, on the resulting film, a silicon carbide
support frame (having the shape of a ring of 75 mm in
10 inner diameter, 90 mm in outer diameter and 5 mm in
thickness) was put and pressed under a pressure of
5 kg/cm^2 , and then placed in a sintering furnace
filled with dry nitrogen. Subsequently, the
temperature inside the furnace was maintained at 200°C
15 for 1 hour, and then raised to 1,400°C at a rate of
10°C/min. The furnace was maintained at this
temperature for 1 hour, and then cooled to obtain an X-
ray mask support having a silicon carbide support film
of 2.1 μm in thickness and 9 nm in surface roughness.

20 The silicon carbide film in the X-ray mask
support prepared in the above manner according to the
process of the present invention was cut into a strip
of 10 x 50 mm^2 , and its Young's modulus was measured
using a tensile tester. The Young's modulus was found
25 to be 250 GPa, which was a value enough for the X-ray
mask support film.

1 Example 11

Inside of a 1 liter autoclave made of glass was replaced with dry nitrogen, and charged therein was 0.40 g of KH (100 mmol; 3.9 mol % based on

5 $\text{CH}_3\text{SiH}_2\text{NH}$).

Tetrahydrofuran (300 ml) was dropwise added with use of a syringe to the inside of the above autoclave, and the mixture was stirred to disperse KH.

Next, using a syringe filled with nitrogen, 15.271 g
10 (0.258 mol) of $(\text{CH}_3\text{SiH}_2\text{NH})_3$ was slowly added to the stirred KH slurry over a period of 15 minutes. After stirring at room temperature for 90 minutes, generation of gas stopped, and a transparent and homogeneous solution remained. Addition thereto of
15 2.28 (16.1 mmol) g of methyl iodide immediately resulted in the formation of a white precipitate of KI. This reaction mixture was further stirred for 30 minutes. Next, most of THF was removed under reduced pressure, and 80 ml of hexane was added to the
20 remaining white slurry. The resulting mixture was subjected to centrifugal separation to separate supernatant liquid from a white solid. This solution was subjected to trap-to-trap distillation, so that 15.1 g (99 % by weight) of white powdery
25 polymethylsilazane was obtained.

A silicon nitride whisker (trade name: SNW,

1 available from Tateho Chemical Industries, Ltd.) of
from 0.1 to 1.5 μm in finess and from 5 to 200 μm in
length was laid up in the same manner as in Example
10. Subsequently, the resulting layup was spray-
5 coated in the same manner as in Example 10, with a
solution obtained by dissolving in toluene 40 % by
weight of the polymethylsilazane synthesized as
described above, thus obtaining a film.

Next, on the resulting film, a silicon carbide
10 support frame having the shape as the frame of Example
10 was put and pressed under a pressure of 5 kg/cm^2 ,
which was placed in a sintering furnace filled with
dry nitrogen. Subsequently, the temperature inside
the furnace was raised to 1,300°C at a rate of
15 5°C/min. The furnace was maintained at this
temperature for 4 hours, and then cooled to obtain an
X-ray mask support having a silicon carbide support
film of 2.9 μm in thickness and 8 nm in surface
roughness.

20 Young's modulus of the silicon carbide film in
the X-ray mask support prepared in the above manner
according to the process of the present invention was
measured in the same manner as in Example 10. The
Young's modulus was found to be 220 GPa, which was a
25 value enough for the X-ray mask support film.

1 Example 12

 An X-ray mask support was obtained in the same manner as in Example 10 except that silicon carbide particles having an average particle diameter of 0.45
5 μm (grade: DUA-1, available from Showa Denko KK) were used in place of the silicon carbide whisker.

 A support film in the resulting support showed good properties like the support film obtained in Example 10.

10 Example 13

 An X-ray mask support was obtained in the same manner as in Example 11 except that silicon nitride particles having an average particle diameter of 0.2
15 μm (grade: SNE-10, available from Ube Industries, Ltd.) were used in place of the silicon nitride whisker.

 A support film in the resulting support showed good properties like the support film obtained in Example 11.

20 Reference Example 1

 Polysilastyrene (trade name: S-400, available from NIPPON SODA CO., LTD.) was dissolved in toluene to prepare a solution of 10 wt/v% in concentration. A surface-polished carbon substrate
25 was set on a spinner (Mikasa Spinner 1H-2) and rotated at 400 rpm, on which the above solution was dropped,

1 thus preparing a film of 31 μm thick.

Next, the resulting film was sintered in the same manner as in Example 10 to obtain an X-ray mask support film.

5 Young's modulus of the film was measured in the same manner as in Example 10. The Young's modulus was found to be 200 GPa, which is a value lower than that of the films obtained in Examples of the present invention.

10 Young's moduli of the support films in the X-ray mask supports prepared in the above Examples were 200 GPa to 250 GPa (in SiC) and 200 GPa to 220 GPa (in SiN); thermal expansion coefficients of the support films and support frames were 4×10^{-6} to $1 \times 10^{-5} \text{K}^{-1}$
15 (in SiC) and 3×10^{-6} to $1 \times 10^{-5} \text{K}^{-1}$ (in SiN); and thermal conductivities were 80 W/m·K (in the case of SiC) and 20 W/m·K (in the case of SiN).

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¹ CLAIMS:

1. An X-ray mask support comprising a support frame and a support film, wherein both of said support frame and support film have a thermal expansion
⁵ coefficient of not more than $1 \times 10^{-5} \text{K}^{-1}$.

2. The X-ray mask support of Claim 1, wherein Young's modulus of said support film is uniform over the whole of said film.

10

3. The X-ray mask support of Claim 1, wherein Young's modulus of said support film is not less than 10 GPa.

15 4. The X-ray mask support of Claim 1, wherein said support film has a uniform film thickness over the whole of said film.

5. The X-ray mask support of Claim 1, wherein
20 said support film has a film thickness of from 1 to 5 μm .

6. The X-ray mask support of Claim 1, wherein said support film has a film thickness of from 2 to 4
25 μm .

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- 1 7. The X-ray mask support of Claim 1, wherein
said support film has a surface roughness at least on
the mask surface, of not more than 10 nm r.m.s.
- 5 8. The X-ray mask support of Claim 1, wherein
said support frame and support film have a thermal
conductivity of not less than 4 W/m.K.
9. The X-ray mask support of Claim 1, wherein
10 said support frame and support film comprise a
compound selected from the group consisting of silicon
carbide, silicon nitride, sialon, carbon and graphite.
10. The X-ray mask support of Claim 1, wherein
15 said support frame and support film independently
comprise a material selected from the group consisting
of silicon carbide and silicon nitride.
11. The X-ray mask support of Claim 1, wherein
20 said support frame comprises the same material as that
of said support film, said material being selected
from the group consisting of silicon carbide and
silicon nitride.
- 25 12. An X-ray mask support comprising a support
frame and a support film, wherein the thermal





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- 48 -

1 expansion coefficient of said support film does not
exceed the thermal expansion coefficient of said
support frame.

5 13. The X-ray mask support of Claim 12,
wherein both of said support frame and support film
have a thermal expansion coefficient of not more than
 $1 \times 10^{-5} \text{K}^{-1}$.

10 14. The X-ray mask support of Claim 12,
wherein Young's modulus of said support film is
uniform over the whole of said film.

15 15. The X-ray mask support of Claim 12,
wherein Young's modulus of said support film is not
less than 10 GPa.

20 16. The X-ray mask support of Claim 12,
wherein said support film has a uniform film thickness
over the whole of said film.

25 17. The X-ray mask support of Claim 12,
wherein said support film has a film thickness of from
1 to 5 μm .

18. The X-ray mask support of Claim 12,

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1 45erein said support film has a film thickness of from
2 to 4 μm .

19. The X-ray mask support of Claim 12,
5 wherein said support film has a surface roughness at
least on the mask surface, of not more than 10 nm
r.m.s.

20. The X-ray mask support of Claim 12,
10 wherein said support frame and support film have a
thermal conductivity of not less than 4 W/m.K.

21. The X-ray mask support of Claim 12,
wherein said support frame and support film comprise a
15 compound selected from the group consisting of silicon
carbide, silicon nitride, sialon, carbon and graphite.

22. The X-ray mask support of Claim 12,
wherein said support frame and support film
20 independently comprise a material selected from the
group consisting of silicon carbide and silicon
nitride.

23. The X-ray mask support of Claim 12,
25 wherein said support frame comprises the same
material as that of said support film, said material





1 being selected from the group consisting of silicon
carbide and silicon nitride.

24. An X-ray mask support comprising a support
5 frame and a support film, wherein both said support
frame and said support film have a thermal expansion
coefficient of not more than $1 \times 10^{-5} \text{K}^{-1}$ and said
support film has a surface roughness at least on the
mask surface, of not more than 10 nm r.m.s.

10

25. The X-ray mask support of Claim 24,
wherein Young's modulus of said support film is
uniform over the whole of said film.

15

26. The X-ray mask support of Claim 24,
wherein Young's modulus of said support film is not
less than 10 GPa.

20

27. The X-ray mask support of Claim 24,
wherein said support film has a uniform film thickness
over the whole of said film.

28. The X-ray mask support of Claim 24,
wherein said support film has a film thickness of from
25 1 to 5 μm .





1 29. The X-ray mask support of Claim 24,
wherein said support film has a film thickness of from
2 to 4 μm .

5 30. The X-ray mask support of Claim 24,
wherein said support frame and support film have a
thermal conductivity of not less than 4 W/m.K.

 31. The X-ray mask support of Claim 24,
10 wherein said support frame and support film comprise a
compound selected from the group consisting of silicon
carbide, silicon nitride, sialon, carbon and graphite.

 32. The X-ray mask support of Claim 24,
15 wherein said support frame and support film
independently comprise a material selected from the
group consisting of silicon carbide and silicon
nitride.

20 33. The X-ray mask support of Claim 24,
wherein said support frame comprises the same material
as that of said support film, said material selected
from the group consisting of silicon carbide and
silicon nitride.

25

34. A process for preparing an X-ray mask





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- 52 -

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1 support film, comprising the steps of forming a film
on a substrate, and sintering said film.

35. The process of Claim 34, wherein said
5 sintering is carried out in an inert gas atmosphere.

36. The process of Claim 34, wherein said film
comprises an organosilicon polymer or pitch.

10 37. The process of Claim 34, wherein the
surface of said substrate has a surface roughness of
not more than 10 nm r.m.s.

38. The process of Claim 34, wherein said
15 substrate has a thermal resistance to not less than
1,400°C.

39. The process of Claim 34, wherein said
substrate has a thermal resistance to not less than
20 1,500°C.

40. The process of Claim 34, wherein said
substrate is decomposed or melted at from 500 to
600°C.

25

41. The process of Claim 34, which comprises

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1 the step of irradiating light before said sintering to
bring a film composition to cross-link.

42. The process of Claim 34, which further
5 comprises the step of removing said substrate.

43. A process for preparing an X-ray mask
support film, comprising the steps of forming a film
on a substrate comprising a compound having the same
10 component unit as that of a sintered product of said
film, and sintering said film.

44. The process of Claim 43, wherein said
sintering is carried out in an inert gas atmosphere.
15

45. The process of Claim 43, wherein said film
comprises an organosilicon polymer or pitch.

46. The process of Claim 43, wherein said
20 substrate has a surface roughness of not more than 0.5
 μm r.m.s.

47. The process of Claim 43, wherein said film
has a film thickness of from 1 to 3 μm .
25

48. A process for preparing an X-ray mask

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- 1 support film, comprising the steps of forming on a
substrate a film containing fibers and/or particles
comprising a compound having the same component unit
as that of a sintered product of said film, and
5 sintering said film.

49. The process of Claim 48, wherein said
fibers and particles comprise silicon carbide, silicon
nitride, sialon, carbon or graphite.

10

50. The process of Claim 48, wherein said
fiber has a fineness of from 0.05 to 1.5 μm .

51. The process of Claim 48, wherein said
15 particles have a particle diameter of not more than 3
 μm .

52. The process of Claim 48, wherein said
sintering is carried out in an inert gas atmosphere.

20

53. The process of Claim 48, wherein the
surface of said substrate has a surface roughness of
not more than 10 nm r.m.s.

25

54. The process of Claim 48, wherein said
substrate has a thermal resistance to not less than





1 1,400°C.

55. The process of Claim 48, wherein said
substrate has a thermal resistance to not less than
5 1,500°C.

56. The process of Claim 48, wherein said
substrate is decomposed or melted at from 500 to
600°C.

10

57. The process of Claim 48, which comprises
the step of irradiating light before said sintering to
bring a film composition to cross-link.

15 58. The process of Claim 48, which comprises
the step of removing said substrate.

59. A process for preparing an X-ray mask
support comprising a support frame and a support film,
20 comprising the steps of forming a thin film, adhering
a support frame on said thin film, and sintering
these.

60. The process of Claim 59, wherein said
25 sintering is carried out in an inert gas atmosphere.





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1 61. The process of Claim 59, wherein said film
comprises an organosilicon polymer or pitch.

 62. The process of Claim 59, wherein said
5 support frame comprises silicon carbide, silicon
nitride, sialon, carbon or graphite.

 63. The process of Claim 59, wherein said thin
film has a substrate comprising a compound having the
10 same constituent with that of a sintered product of
said thin film.

 64. The process of Claim 59, wherein said thin
film contains fibers and/or particles comprising a
15 compound having the same constituent as that of a
sintered product of said thin film.

 65. A process for preparing an X-ray mask
support comprising a support frame and a support film,
20 comprising the steps of forming a support film by
forming a thin film and sintering it, adhering a
support frame on said support film, and sintering
these.

25 66. The process of Claim 65, wherein said
sintering is carried out in an inert gas atmosphere.

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1 67. The process of Claim 65, wherein said film
comprises an organosilicon polymer or pitch.

 68. The process of Claim 65, wherein said
5 support frame comprises silicon carbide, silicon
nitride, sialon, carbon or graphite.

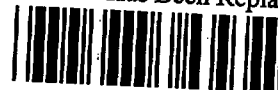
 69. The process of Claim 65, wherein said
support frame is adhered to the support film by using
10 a solution or melt of an organosilicon polymer as an
adhesive.

 70. The process of Claim 65, wherein said thin
film has a substrate comprising a compound having the
15 same constituent as that of a sintered product of said
thin film.

 71. The process of Claim 65, wherein said thin
film contains fibers and/or particles comprising a
20 compound having the same constituent as that of a
sintered product of said thin film.

 72. A process for preparing an X-ray mask
support comprising a support frame and a support film,
25 comprising the steps of integrally molding the support
frame and support film with the same compound to form

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- 58 -

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¹ a molded product, and sintering said molded product.

73. The process of Claim 72, wherein said
sintering is carried out in an inert gas atmosphere.

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74. The process of Claim 72, wherein said film
comprises an organosilicon polymer or pitch.

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