

1 Process for Forming Deposited Film and Process
 for Preparing Semiconductor Device

BACKGROUND OF THE INVENTION

5 Field of the Invention

 This invention relates to a method for forming
deposited film and a method for forming a semiconductor
device. Particularly, it pertains to a method for forming
an Mo deposited film preferably applied to wiring of a
10 semiconductor circuit device, etc. and a semiconductor
device by use of selective deposition Mo film.

Related Background Art

 In the prior art, in electronic devices or
integrated circuits by use of semiconductors, aluminum
15 (Al) or Al-Si etc. have been primarily used for electrodes
and wiring. Here, Al is inexpensive and has high electro-
conductivity, and dense oxidized film can be formed on the
surface. Accordingly, it has many advantages that the
inner portion can be protected to be stabilized, and
20 adhesion to Si is good.

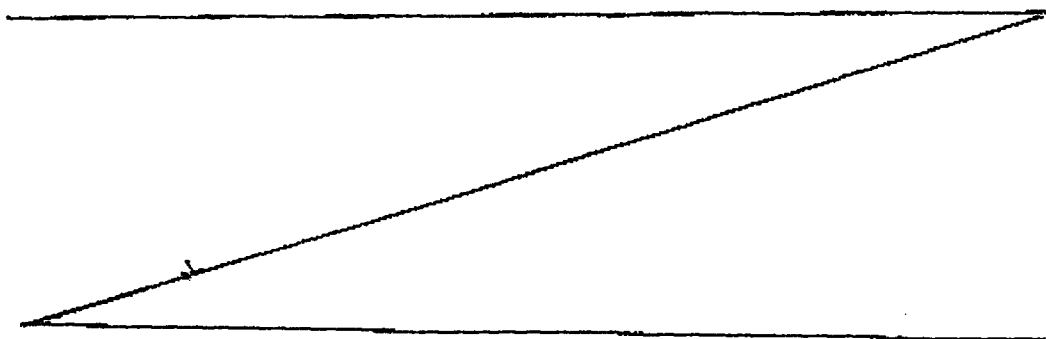
 However, on the other hand, with higher integration,
the self-align technique in which mask matching between
the gate electrode and the diffusion layer, etc. is
unnecessary is indispensable. No metal having low
25 melting point such as Al cannot be used. In the MOS
LSI of the prior art, as the gate electrode wiring

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capable of self-align, a polycrystalline Si doped with an impurity at high concentration has been widely employed. Whereas, with the progress of further higher integration, there ensues the problem that electrical resistance of fine polycrystalline Si wiring, etc. becomes higher. This is vital to high speed actuation of the device. Accordingly, it has been required to have a high melting metal which is lower in volume resistivity than polycrystalline Si and yet is capable of self-align. Also, basically, even when Al can be employed, Si and the wiring Al react with each other during heat treatment at the contact electrode portion with the Si layer, whereby wire breaking or increased resistance of wiring are caused to occur. For this reason, a metal having higher melting point and lower electrical resistance has been employed as the electrode wiring material, and as the barrier metal which prevents the reaction between Si and Al at the contact portion. Particularly, Mo is attracting attention for its sufficiently high melting point (2620 °C) and low electrical resistance ($4.9 \mu\Omega\text{-cm}$).



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1 Deposition methods according to the electron
beam deposition and the sputtering method have been
employed to Mo film used in Mo electrodes wiring, etc.
- of the prior art. With finer dimensional formation by
5 increased integration degree, the surface of LSI, etc.
is subject to excessive unevenness due to oxidation,
diffusion, thin film deposition, and etching, etc.
For example, electrodes or wiring metal must be
deposited on the surface with a stepped difference, or
10 deposited in a via-hole which is fine in diameter and
deep. In 4 Mbit or 16 Mbit DRAM (dynamic RAM), etc.,
the aspect ratio (via hole depth/via hole diameter) of
via-hole in which a wiring metal is to be deposited is
1.0 or more, and the via-hole diameter itself also
15 becomes 1 μm or less. Therefore, even for a via-hole
with large aspect ratio, the technique which can
deposit a wiring metal is required.

Particularly, for performing sure connection
to the device under insulating film such as SiO_2 ,
20 etc., rather than film formation, a metal is required
to be deposited so as to embed only the via-hole of
the device. In such case, a method of depositing a
wiring metal only on Si or metal surface and not
depositing it on an insulating film such as SiO_2 , etc.
25 is required.

It is difficult to achieve such a selective



1 deposition and growth by the electronic beam
deposition and sputter process used in the past. The
sputter process is a physical deposition method
performed by scattering the particles sputtered in
5 vacuum. Therefore, the film thickness becomes very
thin at the step portion and insulating film side
wall, and the breaking of a wire may be caused in an
extreme case. Further, unevenness of a film thickness
and the breaking of a wire cause remarkable
10 degradation of a reliability of LSI.

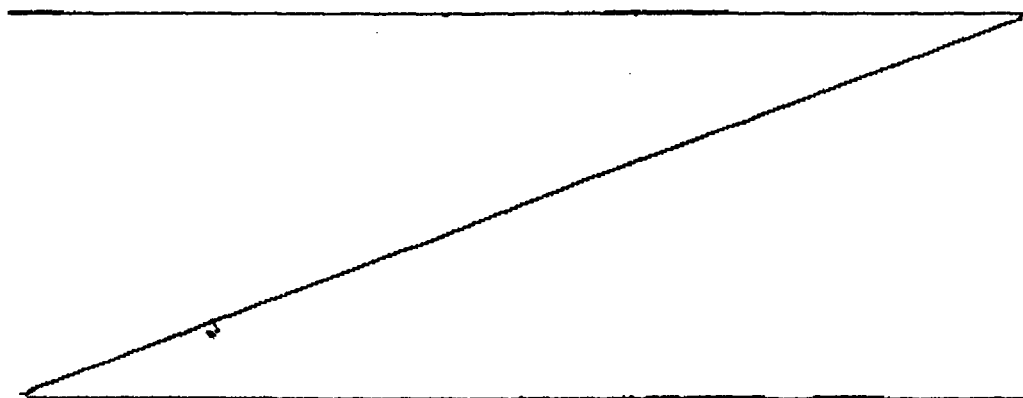
On the other hand, there has been developed
the bias sputtering method in which a bias is applied
on a substrate and deposition is performed so as to
embed Al, Al alloy or Mo silicide only in the via-hole
15 by utilizing the sputter etching action and the
deposition action on the substrate surface. However,
since the bias voltage of some 100 V or higher is
applied on the substrate, deleterious influence occurs
because of charged particle damaging such as change in
20 threshold of MOS-FET, etc. Also, because of presence
of both etching action and deposition action, there is
the problem that the deposition speed cannot be
essentially improved.

In order to solve the problems as described
above, various types of CVD (Chemical Vapor
25 Deposition) methods have been proposed. In these



1 methods, chemical reaction of the starting gas in some
form is utilized. In plasma CVD or optical CVD,
decomposition of the starting gas occurs in gas phase,
and the active species formed there further reacts on
5 the substrate to give rise to film formation. In
these CVD methods, surface coverage on unevenness on
the substrate surface is good since the reaction
occurs in a gaseous phase. However, carbon atoms
contained in the starting gas molecule are
10 incorporated into the film. Also, particularly in
plasma CVD, the problem remained that there was damage
by charged particles (so called plasma damage) as in
the case of the sputtering method.

The thermal CVD method, in which the film
15 grows through the surface reaction primarily on the
substrate surface, is good in surface coverage on
unevenness such as stepped portion of the surface,
etc. Also, it can be expected that deposition within
via-hole will readily occur. Further, wire breaking
20 at the stepped portion can be avoided.



1 For this reason, various studies have been made
about the thermal CVD method as the method for forming
Mo film. For example, there are hydrogen reduction
- method of MoCl_5 and Si reduction method of MoF_6
5 according to normal pressure CVD or reduced pressure
CVD as introduced in Chapter 4 of Handotai Kenkyu
(Semiconductor Research) Vol. 20 (Kogyo Chosakai, 1983).
However, in the hydrogen reduction method of MoCl_5 , a
plurality of molybdenum halide such as MoCl_3 and others
10 other than Mo may be sometimes formed at the portion
other than the substrate surface heated within the
film forming device. Therefore, it is difficult to
control film formation. Also, although film formation
may be possible, no selective deposition can be seen.

15 On the other hand, for example, in EP 147913
(A3) Publication or USP 3,785,862, there is shown the
method of forming Mo film by use of MoF_6 gas, hydrogen
gas and an inert gas.

Whereas, in the Si reduction method of MoF_6 ,
20 MoF_6 reacts in the presence of Si to precipitate Mo,
whereby Si is etched. Therefore, there is a fear that
the electronic circuit on Si wafer may be damaged.
Also, SiO_2 is etched. However, for this reason, in
the Si reduction method of MoF_6 , deposition occurs
25 primarily on Si substrate, and Mo film deposition
dose not occur on SiO_2 at all, but it is clearly
stated in USP 3,785,862 that Mo film is also deposited



1 on SiO_2 . This suggests that selective deposition of
Mo is not so complete. In addition, as described above,
both Si and SiO_2 are subjected to etching, and under such
- state there is a fear that problems may be involved prac-
5 tically concerning surface flatness and mixing of impurity,
etc. As another method, there is an example of normal
pressure CVD method of $\text{Mo}(\text{CO})_6$ as described in Thin
Solid Films, Vol. 63 (1979), p. 169. In this method, Mo
film can be deposited on the substrate by use of normal
10 pressure CVD with Ar as the carrier gas. However, in this
method, there may be sometimes incorporated a considerably
large amount of oxygen and carbon in Mo film as impurities,
and for this reason, there is a fear that electrical
resistance of the deposited film may be increased.
15 Also, according to this method, selective deposition
can be done with difficulty.

As described above, the deposition method of Mo
film of the prior art had many problems to be improved,
such that coverage of the stepped difference of the LSI
20 surface was poor, that the Si surface of LSI was un-
necessarily etched, that damage was given to SiO_2 ,
that deposition reaction could be controlled with
difficulty, or that a large amount of impurities were
mixed into Mo film.



1 SUMMARY OF THE INVENTION

A first object of the present invention is to provide a deposition method of Mo film without giving damage to Si wafer or SiO_2 .

5 A second object of the present invention is to provide a deposition method of Mo film with high stepped difference coverage of LSI surface.

A third object of the present invention is to provide a selective deposition method of Mo film effective
10 for embedding of via-hole, etc.

A fourth object of the present invention is to provide a deposition method of Mo film in which Mo film can be deposited with good controllability.

A fifth object of the present invention is to
15 provide a method for preparing a semiconductor device having characteristics such as excellent surface flatness, migration resistance, etc. by use of the selective deposition method of Mo film for formation of wiring and electrode portions.

20 A sixth object of the present is to a deposited film formation method comprising the steps of:

(a) feeding a gas of an organometallic compound containing molybdenum atom and hydrogen gas onto a substrate having an electron donative surface, and

25 (b) maintaining the temperature of said electron donative surface within the range of the decomposition



1 temperature of said organometallic compound or lower
and 800 °C or lower to form a molybdenum film on said
electron donative surface.

A seventh object of the present invention is
5 to a deposited film formation method comprising the
steps of:

(a) feeding a gas of an organometallic compound
containing molybdenum atom and hydrogen gas onto a
substrate having an electron donative surface and a
10 non-electron donative surface, and

(b) maintaining the temperature of said electron
donative surface within the range of the decomposition
temperature of said organometallic compound or lower and
800 °C or lower to form a molybdenum film selectively
15 on said electron donative surface.

A eighth object of the present invention is to
a method for preparing a semiconductor device comprising
the steps of:

forming a film comprising an insulating material
20 on a semiconductor material,

forming an opening on said film to have said
semiconductor material exposed, and

embedding an electroconductive material in said
opening to form a part of electrical wiring,

25 characterized in that the reaction is carried
out between a gas of an organometallic compound containing



1 molybdenum atom and hydrogen gas at a temperature of the
decomposition temperature of said organometallic compound
or lower and 800 °C or lower to deposit selectively moly-
bdenum on said opening, thereby forming a part of said
5 wiring.

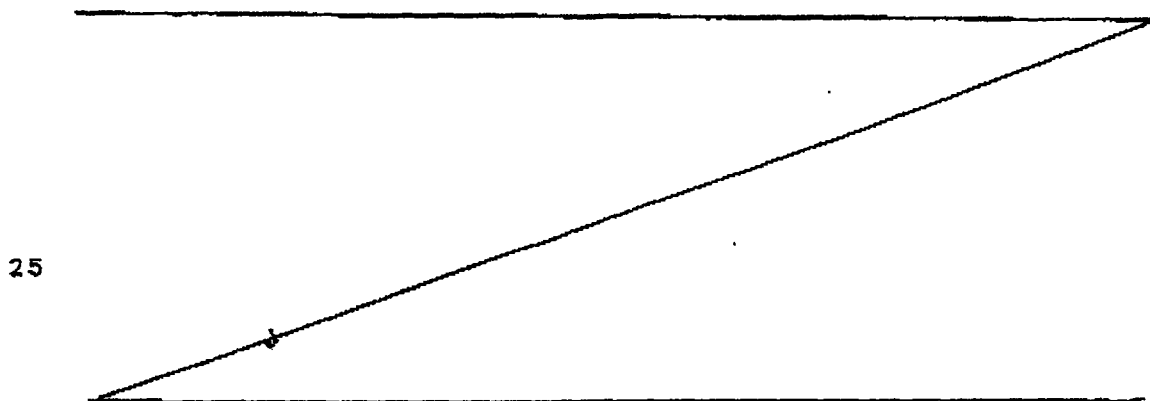
BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a schematic view illustrating an
10 example of a deposition film forming apparatus
possible applicable to the present invention.

Fig. 2 shows a schematic sectional view
illustrating a process for forming a deposition film
according to the present invention.

15 Fig. 3 shows a schematic view illustrating the
other example of a deposition film forming apparatus
possible applicable to the present invention.

Fig. 4 shows a schematic view illustrating a
method for producing a semiconductor device according
20 to the present invention.



11 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferable method for forming the deposited film of the present invention is as described below.

The method for forming the deposited film of the present invention is characterized in that a molybdenum film is formed on an electron donative surface through the reaction with a gas of an organometallic compound containing molybdenum atom and hydrogen gas.

On the other hand, a preferable method for forming the semiconductor device of the present invention is as described below.

The method for forming the semiconductor device of the present invention is characterized in that molybdenum deposits selectively through the reaction between a gas of an organometallic compound containing molybdenum atom and hydrogen gas on a semiconductor surface exposed from an insulating film, thereby forming a part of electrical wiring.

The Mo film obtained by the deposited film formation method according to the present invention contains little impurity such as carbon, etc., and also sufficiently low in electrical resistance. Also, the substrate is free from damage and good in controllability.

And, according to the formation method of deposited film of the present invention, a low resistance, dense Mo film can be selectively deposited on the substrate.

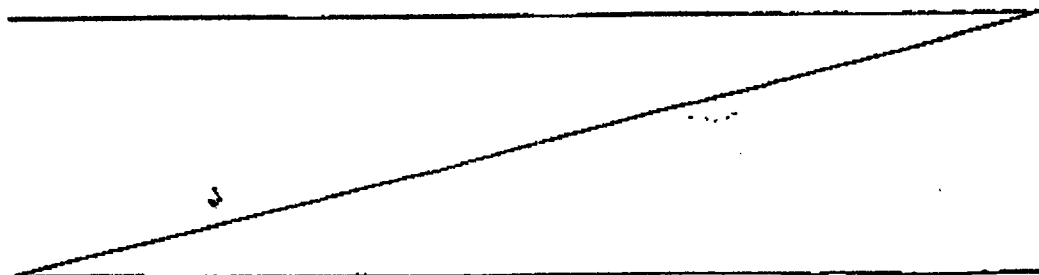


1 Also, by the preparation method of the semi-
conductor device of the present invention, an excellent
semiconductor device by use of a low resistance, dense
and flat Mo film at the wiring portion and the electrode
5 portion can be provided.

 In the present invention, as the starting gases
for deposited film formation, an organic Mo compound
and H_2 gases are employed. By subliming $Mo(CO)_6$,
 $Mo(CH_3)_6$, etc. as the organic Mo compound, which are solid
10 at room temperature and reacting in a carrier gas
such as H_2 , Ar, etc. on a heated substrate, Mo film
is deposited. The detailed mechanism of the reaction
has not been necessarily clarified, but it may be
considered that $Mo(CO)_6$, etc. react with H_2 gas on
15 an electron donative substrate surface such as heated
metal or semiconductor to form Mo. Since this reaction
can proceed with difficulty at the place where the
substrate surface is not electron donative, it may
be considered that deposition of the film occurs
20 with difficulty on a non-electron donative surface.

 Here, electron donative characteristic is
described below in detail.

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1 The electron donative material refers to one
having free electrons existing or free electrons
intentionally formed in the substrate, for example, a
material having a surface on which the chemical
5 reaction is promoted through give-and-take of
electrons with the starting gas molecules attached on
the substrate surface. For example, generally metals
and semiconductors correspond to such material. Those
having very thin oxidized film on the metal or
10 semiconductor surface are also included. For, with
such thin film, the chemical reaction can occur
between the substrate and the attached starting
molecules.

Specifically, there may be included
15 semiconductors such as single crystalline silicon,
polycrystalline silicon, amorphous silicon, etc.,
binary system or ternary system or quaternary system
III-V compound semiconductors comprising combinations
of Ga, In, Al as the group III element and P, As, N as
the group V element, or II-VI compound semiconductors,
20 or metals themselves such as tungsten, molybdenum,
tantalum, aluminum, titanium, copper, etc., or
silicides of the above metals such as tungsten
silicide, molybdenum silicide, tantalum silicide,
25 aluminum silicide, titanium silicide, etc., further
metals containing either one of the constituent of the



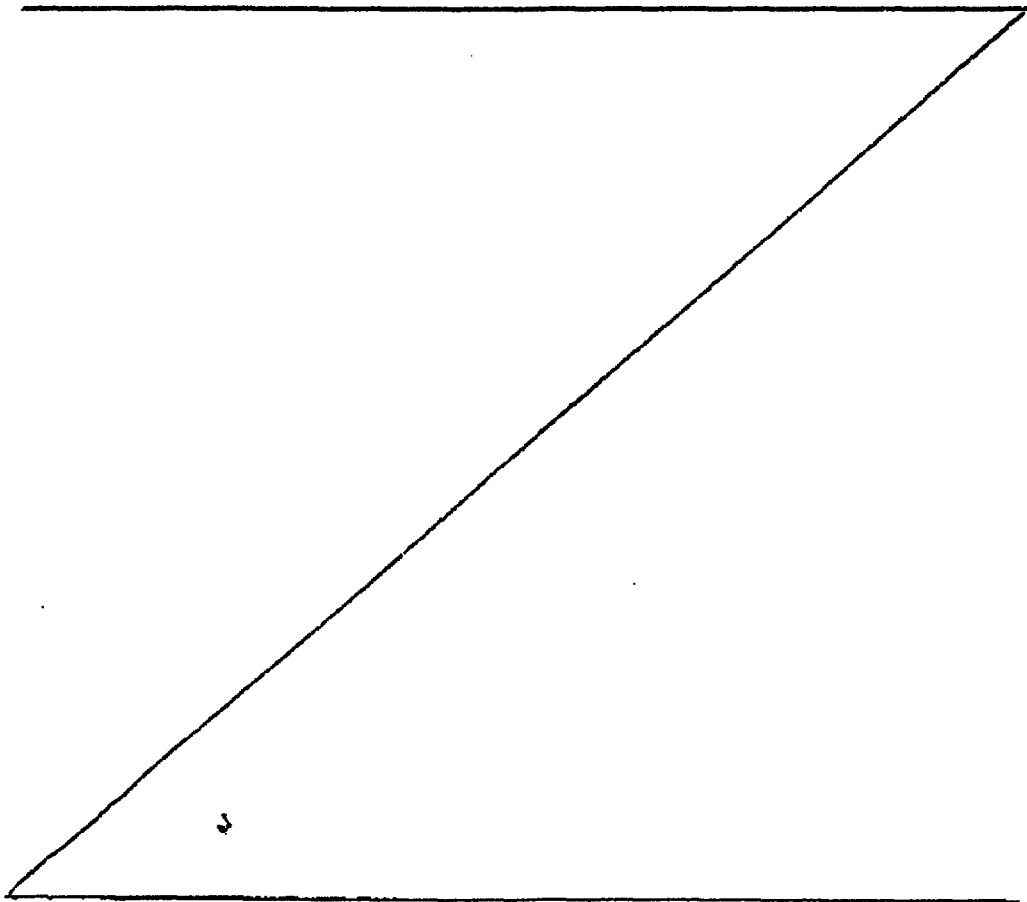
1 above metals such as aluminum silicon, aluminum
titanium, aluminum copper, aluminum tantalum, aluminum
silicon copper, aluminum silicon titanium, aluminum
palladium, titanium nitride, etc.

5 In contrast, the materials for forming the
surface on which Mo is not deposited selectively,
namely the electron non-donative material, are
conventional insulating materials, oxidized silicon
formed by thermal oxidation, CVD, etc., glass or
10 oxidized film such as BSG, PSG, BPSG, etc., thermally
nitrided film, silicon nitrided film by plasma CVD,
low pressure CVD, ECR-CVD method, etc.

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1 Pyrolysis of the starting gas to be used in the
present invention, for example, single substance of
Mo(CO)₆ occurs at around 400 °C, and also partial
decomposition occurs at 300 °C. If the pressure is
5 high and there is no H₂, these decomposed products are
deposited on the substrate without selectivity. Besides,
at this time, a considerably large amount of carbon
and oxygen is incorporated in the Mo film, whereby
electrical resistance becomes higher. Accordingly,
10 also for preventing mixing of impurities into the
film, H₂ Gas is indispensable during the reaction.
At a substrate temperature of 300 °C or higher, when
the pressure of the reaction gas is higher, deposition
of the film is also occur on a non-electron donative
15 surface such as SiO₂, Al₂O₃, etc., whereby selectivity
of deposition is lowered. Hence, no selective deposi-
tion occurs unless the reaction pressure (partial
pressure of organometallic compound) is 100 Torr or
less, and practically it is desirably 10 Torr or less.
20 If the temperature of the substrate is too high, Mo(CO)₆
and H₂ are pyrolyzed abundantly without the aid of an
electron donative surface, whereby impurities in the
film are again increased and also selectivity of
deposition lost. And, no substrate temperature
25 exceeding 800 °C can be employed, and the desirable
substrate temperature is suitably 600 °C or lower.
The most desirable temperature range is from 450 to



1 550 °C. The method has been known in which MoCl_5 , MoF_6
or the like is reduced with H_2 or Si, but in these
methods, halogen elements may be mixed into the film,
or there is damaging such as etching of Si substrate
5 or SiO_2 film, which deteriorate characteristics of the
substrate. For this reason, even the characteristics
of the device by use of this may be sometimes lowered.
On the other hand, according to the method of the
present invention, since no halogen element is used
10 at all, selective deposition of Mo film is possible
without any problem at all as mentioned above. As
the starting gas, other than Mo(CO)_6 , $\text{Mo(CH}_3)_6$ may be
employed. $\text{Mo(CH}_3)_6$ is more desirable than Mo(CO)_6 in
obtaining a film of higher purity. However, organic
15 compounds of Mo are not limited to these at all.

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1 The preferred embodiments of the present
invention are explained below as referring the
drawings. Fig. 1 is a schematic view showing a
deposition film forming apparatus for applying the
5 present invention.

Here, 1 is a substrate for forming Mo film
film. The substrate 1 is mounted on a substrate
holder 3 provided internally of the reaction tube 2
for forming a space for formation of a deposited film
10 which is substantially closed as shown in Fig. 1. As
the material constituting the reaction tube 2, quartz
is preferable, but it may be also made of a metal.
Further, it is preferable to cool the reaction tube.
The substrate holder 3 is made of a metal, and is
15 provided with a heater 4 so that the substrate mounted
thereon can be heated. And, the constitution is made
so that the substrate temperature can be controlled by
controlling the heat generation temperature of the
heater 4.

20 The feeding system of gases is constituted as
described below.

5 is a gas mixer, in which the starting gas
and the reaction gas are mixed, and the mixture is fed
into the reaction tube 2. 6 is a starting gas
25 gasifier provided for gasification of an organic metal
as the starting gas.



1 The organic metal to be used in the present
invention is solid at room temperature, and is formed
into saturated vapor by sublimating the organic metal
- by passing a carrier gas through around the metal
5 within the gasifier 6, which is in turn introduced
into the mixer 5.

At this time, the sublimation is markedly
accelerated by heating the gas or organic metal
itself.

10 The evacuation system is constituted as
described below.

7 is a gate valve, which is opened when
performing evacuation of a large volume such as during
evacuation internally of the reaction tube 2 before
15 formation of the deposited film. 8 is a slow leak
valve, which is used when performing evacuation of a
small volume such as in controlling the pressure
internally of the reaction tube 2 during formation of
the deposited film. 9 is an evacuation unit, which is
20 constituted of a pump for evacuation such as turbo
molecular pump, etc.

The conveying system of the substrate 1 is
constituted as described below.

10 is a substrate conveying chamber which can
25 house the substrate before and after formation of the
deposited film, which is evacuated by opening the



1 valve 11. 12 is an evacuation unit for evacuating the
conveying chamber, which is constituted of a pump for
evacuation such as turbo molecular pump, etc.

The valve 13 is opened only when the substrate
5 1 is transferred between the reaction chamber and the
conveying space.

As shown in Fig. 1, in the gas formation
chamber 6 for forming the starting gas, for example,
the gas formation chamber 6 is maintained at room
10 temperature or the heated solid organic Mo compound is
bubbled with H_2 or Ar (or other inert gas) as the
carrier gas to form gaseous organic Mo compound, which
is transported to the mixer 5. The H_2 gas as the
reaction gas is transported through another route into
15 the mixer 5. The gases are controlled in flow rates
so that the respective partial pressures may become
desired values.

$Mo(CO)_6$ or $Mo(CH_3)_6$ is preferred as the
starting gas. Also $Mo(CO)_6$ and $Mo(CH_3)_6$ may be used
20 in a mixture.

Figs. 2A to 2E are schematic views showing the
state of growing an Mo film in case that the present
invention is employed to a selective formation of Mo
film.

25 Fig. 2A is an illustration showing
schematically the cross-section of the substrate



1 before formation of the Mo deposited film according to
the present invention. 90 is the substrate comprising
an electron donative material, and 91 a thin film
comprising an electron non-donative material.

5 When Mo(CO)_6 as the starting gases and a gas
mixture containing H_2 as the reaction gas are fed onto
the substrate heated within a range from the
decomposition temperature of Mo(CO)_6 or less and 800°C
or less, Mo is precipitated on the substrate 90 other
10 than the thin film 91 comprising the election non-
donative material, whereby a continuous film of Mo is
formed as shown in Fig. 2B. Here, the pressure within
the reaction tube 2 should be desirably 10^{-3} to 760
Torr, and the Mo(CO)_6 partial pressure preferably 1.0
15 $\times 10^{-5}$ to 1.5×10^{-3} -fold of the pressure within the
above reaction tube.

When deposition of Mo is continued under the
above conditions, via the state of Fig. 2C, the Mo
film grows to the level of the uppermost portion of
20 the thin film 91 as shown in Fig. 2D.

As the result of analysis according to Auger's
electron spectroscopy or photoelectric spectroscopy,
no entrainment of an impurity such as carbon or oxygen
is recognized in this film.

25 The deposited film thus formed has a
resistivity of, for example, with a film thickness of



1 600 Å, 8 - 30 $\mu\text{ohm}\cdot\text{cm}$ at room temperature which is far
close to the bulk resistivity of Mo and lower than the
resistivity of polycrystalline Si, and becomes
continuous and flat film. The reflectance in the
5 visible wavelength region is approximately 70-80 %,
and a thin film with excellent surface flatness can be
deposited.

The substrate temperature in forming
deposited film should be desirably the decomposition
10 temperature of the starting gas containing Mo or
higher, e.g. 350 °C or more and 800 °C or lower as
mentioned above, but specifically a substrate
temperature of 400 to 600 °C is desirable in case of
Mo(CO)₆, and a substrate temperature of 350 - 550°C is
15 desirable in case of Mo(CH₃)₆.

A more preferable substrate temperature
condition is 450 °C to 550 °C in case of Mo(CO)₆ and
400°C to 500°C in case of Mo(CH₃)₆. The Mo film
deposited under the this condition contains no carbon
20 and oxygen and is sufficiently low in the resistance.

In the apparatus shown in Fig. 1, Mo can be
deposited on only one sheet of substrate in deposition
for one time. Although a deposition speed of ca. 100
Å/min. can be obtained, it is still insufficient for
25 performing deposition of a large number of sheets
within a short time.

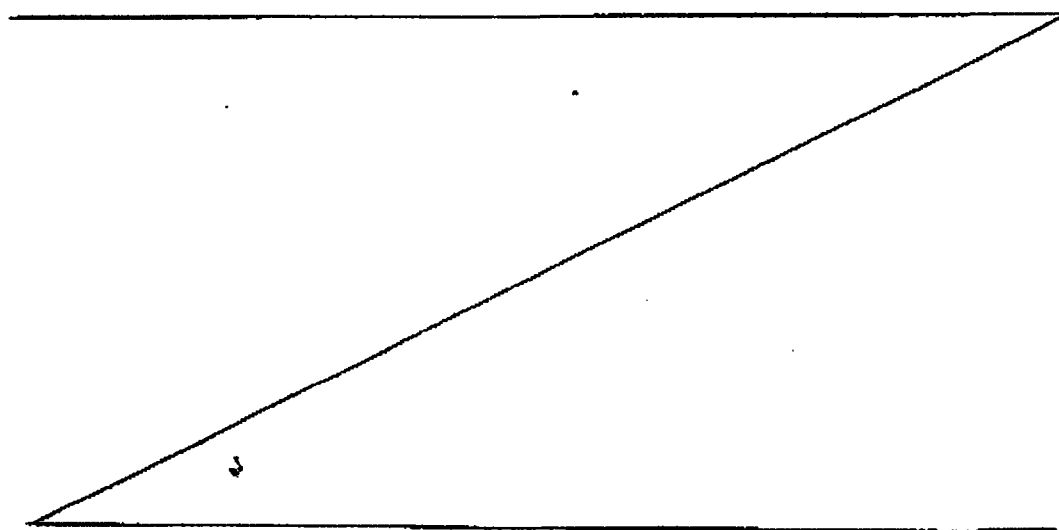


1 As the deposition film forming apparatus for
improving this point, there is the low pressure CVD-
apparatus which can deposit Mo by simultaneous
- mounting of a large number of sheets of wafer. Since
5 the Mo deposition according to the present invention
utilizes the surface reaction of the heated electron
donative substrate surface, for example, in the hot
wall type low pressure CVD method wherein only the
substrate is heated, an Mo compound can be desirably
10 deposited with Mo(CO)_6 and H_2 .

As the conditions of forming the deposited
film, the reaction tube pressure may be 10^{-3} to 760
Torr, desirably 0.1 to 5 Torr, the substrate
temperature 350°C to 800°C , desirably 400°C to 600°C ,
15 $^\circ\text{C}$, the Mo(CO)_6 partial pressure 1×10^{-5} -fold to 1.5
 $\times 10^{-3}$ -fold of the pressure in the reaction tube. And
under these conditions, Mo can be deposited on only
the electron donative substrate.

20

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1 Fig. 3 is a schematic view showing a deposited
film formation apparatus to which such present invention
is applicable.

5 57 is a substrate for forming an Mo film.
50 is an outside reaction tube made of quartz for
forming a space for formation of deposited film which
is substantially closed with respect to surrounding.
51 is an inside reaction tube made of quartz located
for separation of the gas flow within the outside
10 reaction tube 50, 54 a flange made of a metal for
opening and closing the opening of the outside reaction
tube 50, and the substrate 57 is located within the
substrate holding member 56 provided internally of
the inside reaction tube 51. The substrate holding
15 member 56 should be desirably made of quartz.

Also, the present apparatus can control the
substrate temperature by the heater portion 59.
It is constituted so that the pressure internally of
the reaction tube 50 is controllable by the evacuation
20 system bound through the gas evacuation outlet 53.

The present apparatus has a first gas system,
a second gas system and a mixer (all are not shown)
similarly as in the apparatus shown in Fig. 1, and the
starting gases are introduced into the reaction tube
25 50 through the starting gas introducing inlet 52.
The starting gases react on the surface of the
substrate 57 when passing through the inner portion



1 of the inside reaction tube 51 as shown by the arrowhead
58 in Fig. 3 to deposit Mo on the substrate surface 57.
The gases after the reaction pass through the gap portion
- formed by the inside reaction tube 51 and the outside
5 reaction tube 50 and are discharged through the gas
discharging outlet 53.

In taking in and out the substrate, the flange
54 made of a metal is ascended and descended by an
elevator (not shown) together with the substrate
10 holding member 56 and the substrate 57 to move to
a predetermined position, thereby performing attach-
ment and detachment of the substrate.

By forming a deposited film under the conditions
as mentioned above by use of such apparatus, Mo film
15 of good quality can be formed at the same time in
all the wafers within the apparatus.

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1 The present invention is explained below by
giving Examples.

Example 1

First, the procedure for Mo film formation is
5 as follows. By use of the apparatus shown in Fig. 1,
the reaction tube 2 is internally evacuated to ca. 1×10^{-8} Torr by the evacuation unit 9. However, Mo film
can be also formed if the vacuum degree within the
reaction tube 2 may be worse than 1×10^{-8} Torr.
10 After cleaning of substrate such as Si wafer, etc.,
the conveying chamber 10 was released to atmospheric
pressure and Si wafer was mounted in the conveying
chamber. The conveying chamber was evacuated to ca. 1×10^{-6} Torr, and then the gate valve 13 was opened and
15 the substrate was mounted on the wafer holder 3.
Next, the gate valve 13 was closed, and the reaction
chamber 2 was evacuated to a vacuum degree of ca. 1×10^{-8} Torr.

In this Example, Mo(CO)_6 was sublimed to feed
20 through the first gas line. H_2 was used to the
carrier gas of Mo(CO)_6 line. The second gas line was
used for H_2 .

By passing H_2 through the second gas line, the
pressure within the reaction tube 2 was made a
25 predetermined value by controlling the opening of the
slow leak valve 8. Then, the substrate was heated by



1 current passage through the heater 4. After the
substrate temperature has reached a predetermined
temperature, Mo(CO)_6 was introduced into the reaction
tube through the Mo(CO)_6 line. Here the total
5 pressure was ca. 1.5 Torr within the reaction tube,
and the Mo(CO)_6 partial pressure was made ca. 1.5×10^{-4} Torr. Next, when Mo(CO)_6 was introduced into the
reaction tube 2, Mo was deposited. After a
predetermined deposition time has elapsed, feeding of
10 Mo(CO)_6 was stopped. Next, heating of the heater 4
was stopped to cool the substrate. Feeding of H_2 gas
was stopped, and after evacuation internally of the
reaction tube, the substrate was transferred to the
conveying chamber, and only the conveying chamber was
15 made atmospheric before taking out the substrate. The
outline of Mo film formation is as described above.

After preparing monocrystalline Si substrates
as the samples, Mo films were deposited at the
respective substrate temperatures according to the
same procedure as described above under the following
20 conditions:

Total pressure: 1.5 Torr

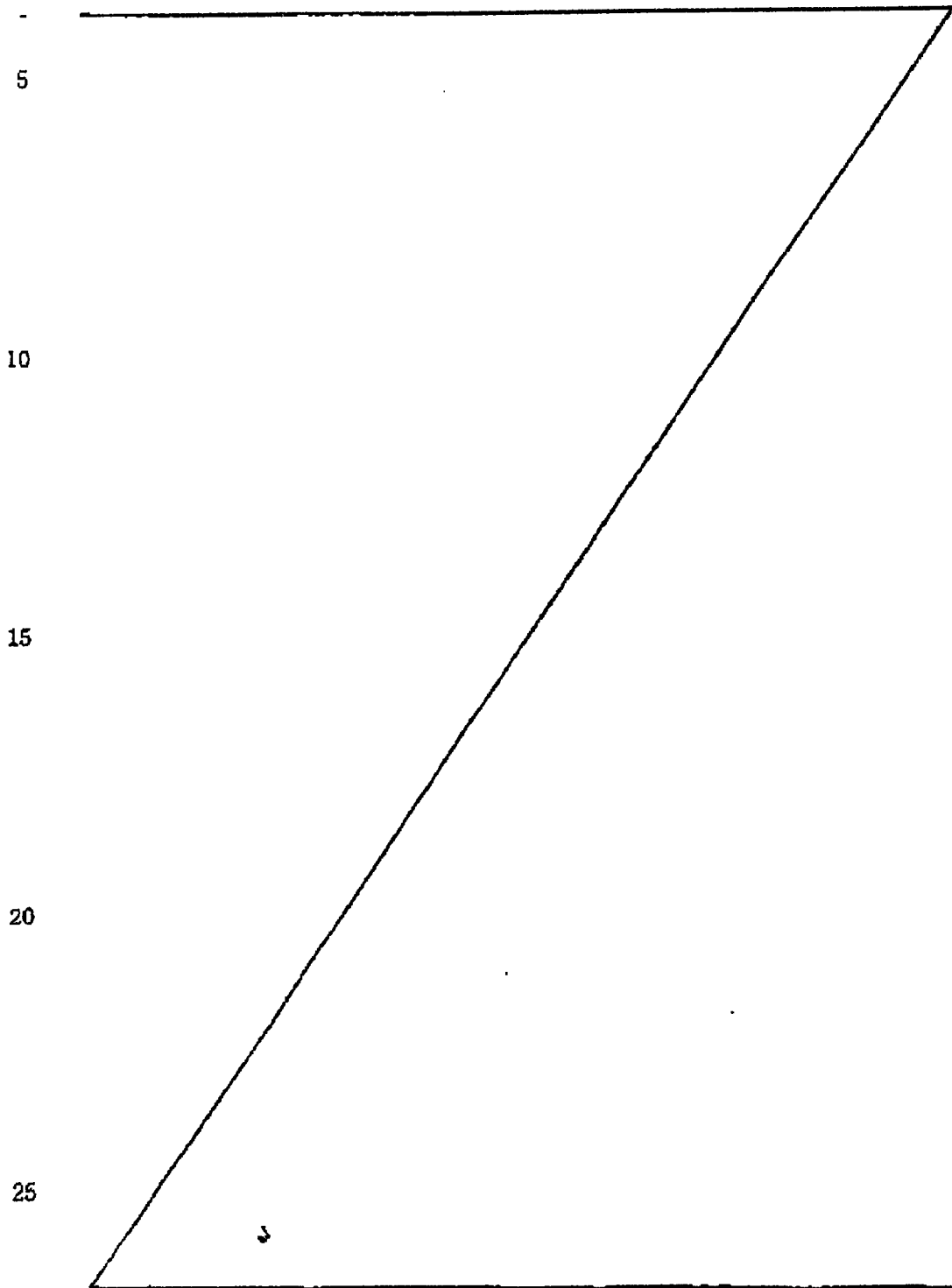
Mo(CO)_6 partial pressure: 1.5×10^{-4} Torr

The Mo films deposited by varying the
25 substrate temperature were evaluated by use of various
evaluation methods. The results are shown in Table 1.

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1 As to the above examples, Mo of excellent
quality was obtained within the temperature range of
400 to 600 °C.



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1 Example 2

According to the following procedure, Mo film was formed. By the evacuation unit 9, the reaction tube 2 was evacuated internally to ca. 1×10^{-8} Torr.

After cleaning of substrate such as Si wafer, etc. the conveying chamber 10 is released to atmospheric pressure and the Si wafer was mounted in the conveying chamber. The conveying chamber was evacuated to ca. 1×10^{-6} Torr, then the gate valve 13 was opened and the wafer was mounted on the wafer holder 3.

Next, the gate valve 13 was evacuated to a vacuum degree in the reaction chamber 2 of ca. 1×10^{-8} Torr.

15 In this Example, the first gas line was used for $\text{Mo}(\text{CO})_6$. As the carrier gas for the $\text{Mo}(\text{CO})_6$ line, Ar different from Example 1 was employed. The second gas line was used for H_2 .

By passing H_2 through the second gas line, the pressure within the reaction tube 2 was made a predetermined value by controlling the opening of the slow leak valve 8. A typical pressure in this Example was made approximately 1.5 Torr. Then, the wafer was heated by current passage through the heater 4. After the wafer temperature was reached a predetermined



1 temperature, Mo(CO)_6 was introduced into the reaction
tube through the Mo(CO)_6 line. The total pressure
within the reaction tube was ca. 1.5 Torr, and the
Mo(CO)₆ partial pressure is made ca. 1.5×10^{-4} Torr.
5 The Ar partial pressure was made 0.5 Torr. Next, when
 Mo(CO)_6 was introduced into the reaction tube 2, Mo
was deposited. After a predetermined deposition time
was elapsed, feeding of Mo(CO)_6 was stopped. Next,
heating of the heater 4 was stopped to cool the wafer.
10 Feeding of H_2 gas was stopped, and after evacuation
internally of the reaction tube, the wafer was
transferred to the conveying chamber, and only the
conveying chamber was made atmospheric pressure before
taking out the wafer. When Ar as the carrier gas was
15 thus used, the resistivity and carbon content of Mo
film formed were a little high. This is a level
having no problems practically and the result almost
similar to Example 1 was obtained.

Example 3

20 By use of the low pressure CVD apparatus shown
in Fig. 2, Mo film was formed on the substrate with
the constitution as described below.

As the substrate surface material having
electron donative properties, monocrystalline silicon
(monocrystalline Si), polycrystalline silicon
25 (polycrystalline Si), tungsten (W), molybdenum (Mo),



1 tantalum (Ta), tungsten silicide (WSi), titanium
silicide (TiSi), aluminum (Al), aluminum silicon (Al-
Si), titanium aluminum (Al-Ti), titanium nitride (Ti-
N), copper (Cu), aluminum silicon copper (Al-Si-Cu),
5 aluminum palladium (Al-Pd), titanium (Ti), molybdenum
silicide (Mo-Si), tantalum silicide (Ta-Si) were
employed. These samples, Al_2O_3 substrates and SiO_2
glass substrates were placed in the low pressure CVD
apparatus shown in Table 3, and Mo films were formed
10 within the same badge. The film forming conditions
were a reaction tube pressure of 0.2 Torr, an Mo(CO)_6
partial pressure of 1.0×10^{-5} Torr, a substrate
temperature of 450°C .

As the result of film formation under such
15 conditions, deposition of Mo film occurred only on
samples having the electron donative substrate
surface. The film quality of the Mo film was found to
be very good, exhibiting the same properties as one
prepared at a substrate temperature of 450°C shown in
20 Example 1. On the other hand, on both the Al_2O_3
substrate and the SiO_2 glass substrate which are
electron non-donative, no Mo film was deposited at
all.

Example 4

25 Deposited films were formed according to the
same procedure as shown in Example 1 by use of



- 1 $\text{Mo}(\text{CH}_3)_6$ as the starting gas and setting the conditions as follows:

Total pressure: 2.0 Torr

$\text{Mo}(\text{CH}_3)_6$ partial pressure: 2×10^{-4} Torr,

- 5 As this result, in the temperature range of the substrate temperature from 350°C to 550°C , Mo thin films containing very little carbon impurity and having low electrical resistance were deposited in a good selectivity on the substrate similarly as in
10 Example 1.

Example 5

The preparation of samples of this Example is described below.

- 15 Si substrates (N type, $1 - 2 \text{ ohm.cm}$) were subjected to thermal oxidation at a temperature of 1000°C according to the hydrogen combustion system (H_2 : 4 liters/M, O_2 : 2 liters/M).

- 20 The film thickness was $7000 \text{ \AA} \pm 500 \text{ \AA}$, and the refractive index 1.46. A photoresist was coated on the whole Si substrate, and a desired pattern was baked by an exposure machine. The pattern was such that various holes of $0.25 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m} - 100 \text{ }\mu\text{m} \times 100 \text{ }\mu\text{m}$ were opened. After development of the resist, with the photoresist as the mask, the subbing SiO_2 was
25 etched by the reactive ion etching (RIE), etc. to have the substrate Si partially exposed. The samples



1 having various sizes of SiO_2 holes of $0.25 \mu\text{m} \times 0.25$
 $\mu\text{m} - 100 \mu\text{m} \times 100 \mu\text{m}$ were prepared. The deposited film
 was formed on the samples thus formed similarly as in
 Example 1. Specifically the substrate temperature was
 5 changed and Mo film was deposited according to the
 procedure as described above under the following
 conditions:

Total pressure: 1.5 Torr,

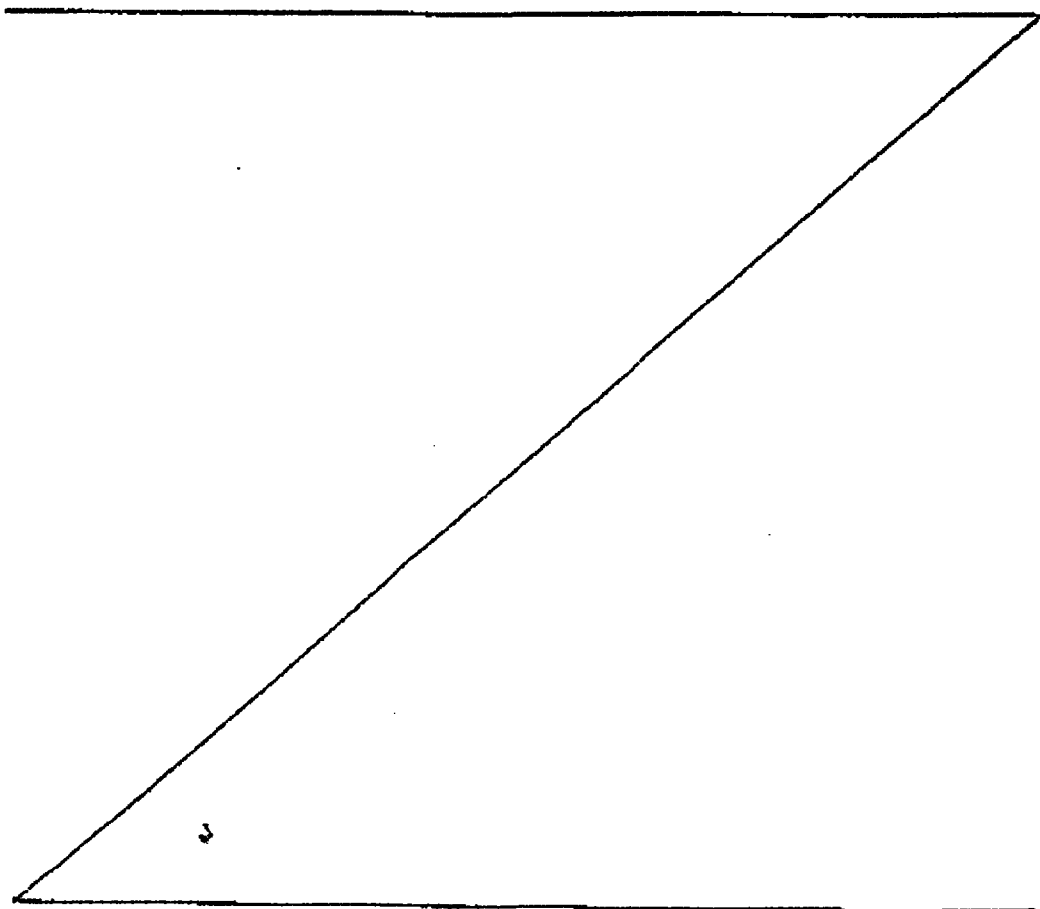
Mo(CO)_6 partial pressure: 1.5×10^{-4} Torr.

10 The Mo films deposited by varying the
 substrate temperature were evaluated by use of various
 evaluation methods. The results are shown in Table 2.

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1 In the result of film formation, Mo was not
deposited on SiO_2 at a temperature range from 400°C to
600°C at all, and Mo was deposited only on the portion
with opening of SiO_2 , i.e. the portion to have Si
5 exposed.

Example 6

By means of the reduced pressure CVD apparatus
shown in Fig. 3, Mo films were formed on the
substrates with the constitutions as described below
10 (Samples 8-1 to 8-179).

Preparation of Sample 8-1

On a monocrystalline silicon as the electron
donative first substrate surface material, a thermally
oxidized SiO_2 film as the electron non-donative second
15 substrate surface material was formed, and patterning
was effected according to the photolithographic steps
as shown in Example 5 to have the monocrystalline
silicon surface partially exposed.

The film thickness of the thermally oxidized
20 SiO_2 film was found to be 7000 Å, with the size of the
exposed portion of the monocrystalline silicon, namely
opening being 3 µm x 3 µm. Thus, Sample 8-1 was
prepared. (Hereinafter, such sample is expressed as
"thermally oxidized SiO_2 (hereinafter abbreviated as T-
25 SiO_2)/monocrystalline silicon").

Preparation of Samples 8-2 to 8-179



1 Sample 8-2 is an oxidized film formed by
normal pressure CVD (hereinafter abbreviated as
SiO₂)/monocrystalline silicon.

 Sample 8-3 is a boron doped oxidized film
5 formed by normal pressure CVD (hereinafter abbreviated
as BSG)/monocrystalline silicon.

 Sample 8-4 is a phosphorus doped oxidized film
formed by normal pressure CVD (hereinafter abbreviated
as PSG)/monocrystalline silicon.

10 Sample 8-5 is a phosphorus and boron doped
oxidized film formed by normal pressure CVD
(hereinafter abbreviated as BSPG)/monocrystalline
silicon.

 Sample 8-6 is a nitrided film formed by plasma
15 CVD (hereinafter abbreviated as P-S:N)/monocrystalline
silicon.

 Sample 8-7 is a thermally nitrided film
(hereinafter abbreviated as T-S:N)/monocrystalline
silicon.

20 Sample 8-8 is a nitrided film formed by low
pressure CVD (hereinafter abbreviated as LP-
S:N)/monocrystalline silicon.

 Sample 8-9 is a nitrided film formed by ECR
apparatus (hereinafter abbreviated as ECR-
25 SiN)/monocrystalline silicon.

 Further, by combinations of the electron



1 donative first substrate surface material and the
electron non-donative second substrate surface
material, Samples 8-11 to 8-179 shown in Table 3 were
prepared. As the first substrate surface material,
5 monocrystalline silicon (monocrystalline Si),
polycrystalline silicon (polycrystalline Si), tungsten
(W), molybdenum (Mo), tantalum (Ta), tungsten silicide
(WSi), titanium silicide (TiSi), aluminum (Al),
aluminum silicon (Al-Si), titanium aluminum (Al-Ti),
10 titanium nitride (Ti-N), copper (Cu), aluminum silicon
copper (Al-Si-Cu), aluminum palladium (Al-Pd),
titanium (Ti), molybdenum silicide (Mo-Si), tantalum
silicide (Ta-Si) were employed. These samples, Al_2O_3
substrates and SiO_2 glass substrates were placed in
15 the low pressure CVD apparatus shown in Table 3, and
Mo films were formed within the same badge. The film
forming conditions were a reaction tube pressure of
0.2 Torr, an Mo(CO)_6 partial pressure of 1.0×10^{-5}
Torr, a substrate temperature of 450°C .

20 As the result of film formation under such
conditions, concerning all the samples applied with
patterning from Sample 8-1 to 8-179, deposition of Mo
film occurred only on the electron donative first
substrate surface to embed completely the opening with
25 the depth of 7000 Å. The film quality of the Mo film
was found to be very good, exhibiting the same



1 properties as one prepared at a substrate temperature
of 450 °C shown in Example 5. On the other hand, on
the second substrate surface which is electron non-
donative, no Mo film was deposited at all, whereby
5 complete selectivity was obtained. On both the Al_2O_3
substrate and the SiO_2 glass substrate which are
electron non-donative, no Mo film was deposited at
all.

Example 7

10 By use of the low pressure CVD apparatus shown
in Fig. 3, Mo film was formed on the substrate with
the constitution as described below.

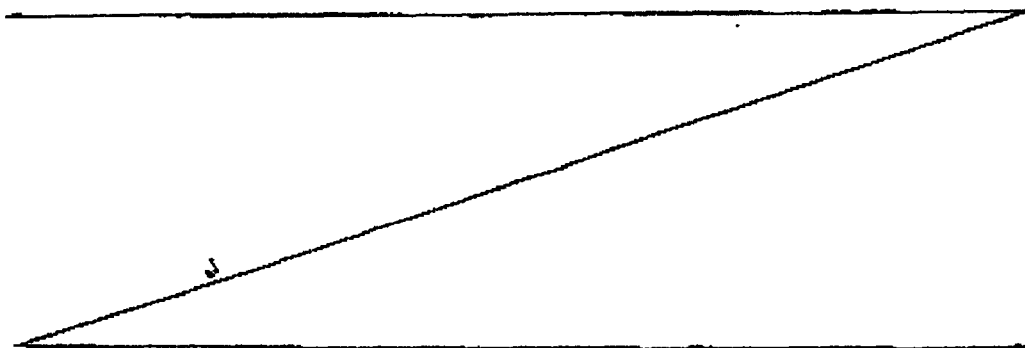
First, a thermally oxidized film as the
electron non-donative second substrate surface
15 material was used. A polycrystalline Si as the
electron donative first substrate surface material was
formed on the thermally oxidized film. Next,
patterning was effected according to the
photolithographic steps as shown in Example 5 to have
the thermally oxidized film surface partially exposed.
20

The film thickness of the polycrystalline silicon at
this time was 2000 Å, with the size of the thermally
oxidized film exposed portion, namely opening being 3
µm x 3 µm. Such sample is called 9-1. By
25 combinations of the electron non-donative second
substrate surface materials (T-SiO₂, CVD-SiO₂, BSG,



1 PSG, BPSG, P-SiN, T-SiN, LP-SiN, ECR-SiN) and the
 electron donative first substrate surface materials
 (polycrystalline Si, monocrystalline Si, Al, W, Mo,
 5 Ta, WSi, TiSi, TaSi, Al-Si, Al-Ti, TiN, Cu, Al-Si-Cu,
 Al-Pd, Ti, Mo-Si), Samples of 9-1 to 9-169 shown in
 Table 4 were prepared. These samples were placed in
 the low pressure CVD apparatus shown in Fig. 3, and Mo
 film was formed within the same batch. The film
 forming conditions were a reaction tube pressure of
 10 0.2 Torr, an Mo(CO)_6 partial pressure of 1.0×10^{-5}
 Torr, a substrate temperature of 450°C . As the
 result of film formation under such conditions, in all
 the samples from 9-1 to 9-169, no Mo film was
 deposited at all at the opening having the electron
 15 non-donative second substrate exposed, but Mo of about
 5000 Å was deposited only on the electron donative
 first substrate surface, whereby complete selectivity
 was obtained. The film quality of the Mo film
 deposited was found to be very good, exhibiting the
 20 same properties as one prepared at a substrate
 temperature of 450°C in Example 5.

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1 Example 8

Deposition was carried out according to the same procedure as shown in Example 5 by use of $\text{Mo}(\text{CH}_3)_6$ as the starting gas under the following conditions:

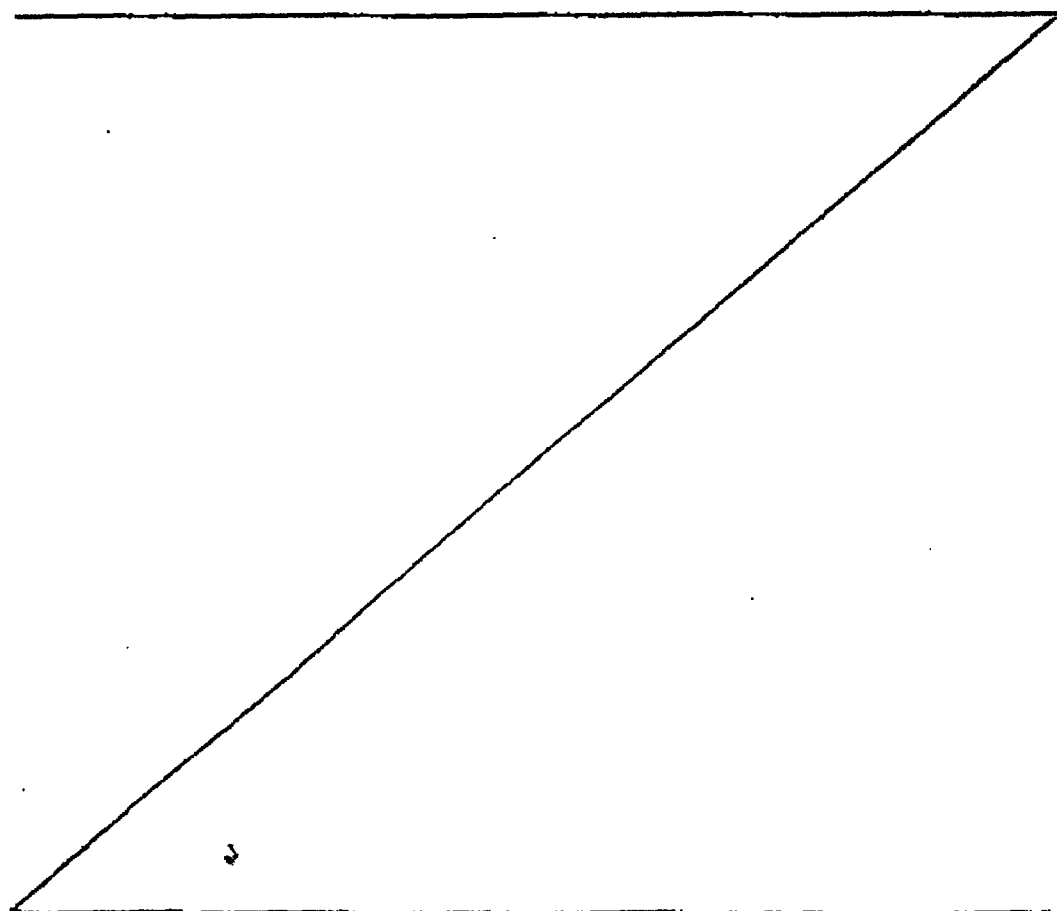
Total pressure: 2.0 Torr

$\text{Mo}(\text{CH}_3)_6$ partial pressure: 3×10^{-4} Torr,
in the temperature range of the substrate temperature from 350 °C to 550 °C. As the result, Mo thin films containing very little carbon impurity and having low electrical resistance were deposited in a good selectivity on the substrate similarly as in Example 5.

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1 Example 9

 As an example for forming source and drain
electrodes of a gate insulating type transistor,
formation of an electrode in a contact hole on a
5 source and a drain was carried out using the film
forming process of the present invention. This is
described with reference to Fig. 4.

 First, on a p-type silicon wafer 501, a thick
field oxidized film and a thin thermal oxidized film 502
10 were formed by use of the usual selective oxidation
process, etc. to the wafer 501 (Fig. 4A).
Subsequently, using SiH_4 gas as a starting material
gas, a polycrystalline silicon layer was formed by
heat CVD method, and a polycrystalline silicon gate
15 electrode 504 was formed by lithography method. At
the same time, phosphorus was self-aligningly injected
using the thick field oxidized film and the gate electrode
504 as a mask to form an impurity-diffused region 505
of $1 \times 10^{18} \text{ cm}^{-3}$ (Fig. 4B). Next, a silicon oxidized
20 film 508 was formed by heat CVD method (Fig. 4C). A
contact hole 509 with a size of $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ was
formed by lithography method (Fig. 4D). The substrate
thus obtained was moved to the apparatus as shown in
Fig. 1 to form an Mo film.

25 Here, the substrate temperature was set to be
450°C. Using $\text{Mo}(\text{CO})_6$ as a starting material gas and



1 H_2 as a carrier gas, an Mo film was formed under
conditions of an $Mn(CO)_6$ partial pressure of 1.5×10^{-4}
Torr and a total pressure of 1.5 Torr.

After the formation of the Mo film was
5 completed, the transistor was taken out of the film
forming apparatus and observed, to confirm that a
Mo film 510 was deposited only on the phosphours-
diffused Si 505 in the contact hole 509, and was not
deposited on the oxidized film 508 (Fig. 4E). The
10 surface of the Mo film 510 was very flat.
Characteristics of the resulting transistor was
examined to reveal that very good characteristics were
exhibited.

It was also possible to form a thin Mo
15 film only on the bottom of the contact hole 509 and
thereafter form on the thin Mo film an Al film
as an electrode material. It was still also possible
to use the Mo film as a barrier metal.

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Table 1

Substrate temperature	300°C	350°C	400°C	450°C	500°C	550°C	600°C	800°C
Deposition on Si	Not deposited	Deposited in small amount	Deposited	Deposited	Deposited	Deposited	Deposited	Deposited
Carbon content	—	—	~ 1 %	Not detected	Not detected	Not detected	1% or lower	~ 1 %
Resistivity	—	Non-measurement	~150 $\mu\Omega\text{cm}$	8~30 $\mu\Omega\text{cm}$				

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Table 2

Substrate temperature	300°C	350°C	400°C	450°C	500°C	550°C	600°C	800°C
Deposition on Si	Not deposited	Deposited in small amount	Deposited	Deposited	Deposited	Deposited	Deposited	Deposited
Carbon content	—	—	~ 1 %	Not detected	Not detected	Not detected	1% or lower	~ 1 %
Resistivity	—	Non-measurable	~150 $\mu \Omega \text{ cm}$	8 ~ 30 $\mu \Omega \text{ cm}$				
Deposition on oxide film	Not deposited	Not deposited	Not deposited	Not deposited	Not deposited	Not deposited	Deposited in small amount	Not deposited

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Table 3 (No. 1)

	Monocry- stalline Si	Polycry- stalline Si	W	Mo	Ta	WSi	TiSi	Al	Al Si
T-SiO ₂	8-1	8-11	8-31	8-41	8-51	8-61	8-71	8-81	8-91
SiO ₂	8-2	8-12	8-32	8-42	8-52	8-62	8-72	8-82	8-92
BSG	8-3	8-13	8-33	8-43	8-53	8-63	8-73	8-83	8-93
PSG	8-4	8-14	8-34	8-44	8-54	8-64	8-74	8-84	8-94
BPSG	8-5	8-15	8-35	8-45	8-55	8-65	8-75	8-85	8-95
P-SiN	8-6	8-16	8-36	8-46	8-56	8-66	8-76	8-86	8-96
T-SiN	8-7	8-17	8-37	8-47	8-57	8-67	8-77	8-87	8-97
LP-SiN	8-8	8-18	8-38	8-48	8-58	8-68	8-78	8-88	8-98
ECR-SiN	8-9	8-19	8-39	8-49	8-59	8-69	8-79	8-89	8-99

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Table 3 (No. 2)

	Al Ti	Ti-N	Cu	Al -Si-Cu	Al Pd	Ti	Mo-Si	Ta-Si
T-SiO ₂	8-101	8-111	8-121	8-131	8-141	8-151	8-161	8-171
SiO ₂	8-102	8-112	8-122	8-132	8-142	8-152	8-162	8-172
BSG	8-103	8-113	8-123	8-133	8-143	8-153	8-163	8-173
PSG	8-104	8-114	8-124	8-134	8-144	8-154	8-164	8-174
BPSG	8-105	8-115	8-125	8-135	8-145	8-155	8-165	8-175
P-SiN	8-106	8-116	8-126	8-136	8-146	8-156	8-166	8-176
T-SiN	8-107	8-117	8-127	8-137	8-147	8-157	8-167	8-177
LP-SiN	8-108	8-118	8-128	8-138	8-148	8-158	8-168	8-178
ECR-SiN	8-109	8-119	8-129	8-139	8-149	8-159	8-169	8-179

Note: Numeral indicates Sample No.



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Table 4 (No. 1)

	Monocry- stalline Si	Polycry- stalline Si	W	Mo	Ta	WSi	TiSi	Al	AlSi
T-SiO ₂	9-1	9-11	9-31	9-41	9-51	9-61	9-71	9-81	9-91
SiO ₂	9-2	9-12	9-32	9-42	9-52	9-62	9-72	9-82	9-92
BSG	9-3	9-13	9-33	9-43	9-53	9-63	9-73	9-83	9-93
PSG	9-4	9-14	9-34	9-44	9-54	9-64	9-74	9-84	9-94
BPSG	9-5	9-15	9-35	9-45	9-55	9-65	9-75	9-85	9-95
P-SiN	9-6	9-16	9-36	9-46	9-56	9-66	9-76	9-86	9-96
T-SiN	9-7	9-17	9-37	9-47	9-57	9-67	9-77	9-87	9-97
LP-SiN	9-8	9-18	9-38	9-48	9-58	9-68	9-78	9-88	9-98
ECR-SiN	9-9	9-19	9-39	9-49	9-59	9-69	9-79	9-89	9-99

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Table 4 (No. 2)

	AlTi	Ti-N	Cu	Al-Si-Cu	AlPd	Ti	Mo-Si	Ta-Si
T-SiO ₂	9-101	9-111	9-121	9-131	9-141	9-151	9-161	9-171
SiO ₂	9-102	9-112	9-122	9-132	9-142	9-152	9-162	9-172
BSG	9-103	9-113	9-123	9-133	9-143	9-153	9-163	9-173
PSG	9-104	9-114	9-124	9-134	9-144	9-154	9-164	9-174
BPSG	9-105	9-115	9-125	9-135	9-145	9-155	9-165	9-175
P-SiN	9-106	9-116	9-126	9-136	9-146	9-156	9-166	9-176
T-SiN	9-107	9-117	9-127	9-137	9-147	9-157	9-167	9-177
LP-SiN	9-108	9-118	9-128	9-138	9-148	9-158	9-168	9-178
ECR-SiN	9-109	9-119	9-129	9-139	9-149	9-159	9-169	9-179

Note: Numeral indicates Sample No.

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1 WHAT IS CLAIMED IS:

1. A deposited film formation method comprising the steps of:

(a) feeding a gas of an organometallic compound containing molybdenum atom and hydrogen gas onto a substrate having an electron donative surface, and

(b) maintaining the temperature of said electron donative surface within the range of the decomposition temperature of said organometallic compound or lower and 800 °C or lower to form a molybdenum film on said electron donative surface.

2. A deposited film formation method according to Claim 1, wherein said organometallic compound is $\text{Mo}(\text{CO})_6$.

3. A deposited film formation method according to Claim 1, wherein said organometallic compound is $\text{Mo}(\text{CH}_3)_6$.

4. A deposited film formation method according to Claim 1, wherein said electron donative surface comprises a semiconductor.

5. A deposited film formation method comprising the steps of:

(a) feeding a gas of an organometallic compound containing molybdenum atom and hydrogen gas onto a substrate having an electron donative surface and a





1 non-electron donative surface, and

(b) maintaining the temperature of said electron
donative surface within the range of the decomposition
temperature of said organometallic compound or lower
5 and 800 °C or lower to form a molybdenum film selec-
tively on said electron donative surface.

6. A deposited film formation method according
to Claim 5, wherein said organometallic compound is
10 $\text{Mo}(\text{CO})_6$.

7. A deposited film formation method according
to Claim 5, wherein said organometallic compound is
 $\text{Mo}(\text{CH}_3)_6$.

15 8. A deposited film formation method according
to Claim 5, wherein the partial pressure of said
organometallic compound is 100 Torr or lower.

20 9. A method for preparing a semiconductor
device comprising the steps of:
forming a film comprising an insulating material
on a semiconductor material,
forming an opening on said film to have said
25 semiconductor material exposed, and
embedding an electroconductive material in
said opening to form a part of electrical wiring,





1 characterized in that the reaction is carried
out between a gas of an organometallic compound containing
molybdenum atom and hydrogen gas at a temperature of the
decomposition temperature of said organometallic compound
5 or lower and 800 °C or lower to deposit selectively
molybdenum in said opening, thereby forming a part
of said wiring.

10 10. A method for preparing a semiconductor
device according to Claim 9, wherein said organometallic
compound is $\text{Mo}(\text{CO})_6$.

15 11. A method for preparing a semiconductor
device according to Claim 9, wherein said organometallic
compound is $\text{Mo}(\text{CH}_3)_6$.

20 12. A method of forming a film in which molybdenum
is deposited substantially without carbon on an electron
donative surface, from a source of molybdenum to which
the surface is substantially resistant to etching.

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