

INSULATING FILM FOR SEMICONDUCTOR DEVICE AND
SEMICONDUCTOR DEVICE

FIELD OF THE INVENTION

5 The present invention relates to an interlayer insulating film formed on a production process of a semiconductor device, and a semiconductor device using the interlayer insulating film.

10 BACKGROUND OF THE INVENTION

Miniaturization of circuit patterns, low power consumption and high-speed operation of semiconductor devices proceed, and therefore low capacitance and low resistance of the circuit patterns are spread. As one
15 means of ensuring high-speed and normal operation of the circuit, there has been considered to lower a dielectric constant of an interlayer insulating film.

An insulating film containing a carbon atom, such as an amorphous carbon film, an organic compound insulating
20 film containing a fluorine atom, and an inorganic insulating film have drawn attention as an insulating film having a low dielectric constant. However, must satisfy the following requirements to become a substitute of a silicon oxide insulating film, which is most frequently
25 employed at the present. That is, they must have:

- 1) Low dielectric constant,
and also the following characteristics, which are basically required for a semiconductor insulating film:
- 2) Good adhesion,
- 30 3) Good workability,
- 4) Good in step coverage
- 5) Good in gap fill property,

THIS SHEET HAS BEEN
REPLACED

6) Low water absorption

7) Capability of coping with a damascene process
(embedded wiring).

However, no material has been known that has a low
5 dielectric constant and satisfies all the characteristics
required for an interlayer insulating film of a
semiconductor device.

SUMMARY OF THE INVENTION

10 An object of the invention is to provide an insulating
film having a low dielectric constant and exhibiting
performance that is sufficient as an interlayer insulating
film of a semiconductor device, and also provide a
semiconductor device using the insulating film.

15 The object of the invention can be accomplished by the
following constitutions of the invention.

(1) An insulating film for a semiconductor device
used as an interlayer insulating film of a semiconductor
device, the insulating film consisting essentially of poly-
20 α,α -difluoroparaxylylene and having a relative dielectric
constant of from 2.1 to 2.7.

(2) An insulating film for a semiconductor device
used as an interlayer insulating film of a semiconductor
device, the insulating film consisting essentially of poly-
25 α,α -difluoroparaxylylene and exhibiting a step coverage of
from 0.4 to 0.9.

(3) An insulating film for a semiconductor device
capable of being filled in a gap, the insulating film
consisting essentially of poly- α,α -difluoroparaxylylene,
30 having a ratio (D/L) of a depth (D) and an opening width
(L) of 1 or more.

This Sheet Has Been Replaced



(4) An insulating film for a semiconductor device as in one of the constitutions (1) to (3), wherein a shape of the insulating film is capable of being patterned by irradiation of oxygen plasma.

5 (5) A semiconductor device comprising a semiconductor substrate having thereon at least two conductive layers through an interlayer insulating film, the interlayer insulating film is an insulating film as in one of the constitutions (1) to (4).

10

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatic front view of a constitutional example of a LPCVD (Low Pressure Chemical Vapor Deposition) apparatus used for formation of an
15 insulating film of the invention.

Figure 2 is an explanatory diagram of calculation of a step coverage.

Figures 3A to 3C are cross sectional views showing a damascene process.

20 Figure 4 is a cross sectional view showing an embodiment in which an insulating film of the invention is used as an interlayer insulating film of a semiconductor device.

25 Figure 5 is a scanning electron micrograph showing a cross section of a substrate having an insulating film of the invention formed thereon.

Figure 6 is a scanning electron micrograph showing a cross section of a substrate having an insulating film of the invention formed thereon.

30 Figure 7 is a scanning electron micrograph showing a cross section of a substrate having an insulating film of the invention formed thereon.

This Sheet Has Been Replaced



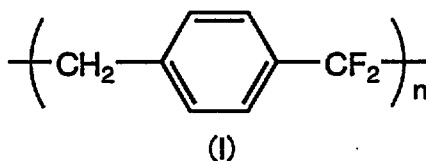
Figure 8 is a scanning electron micrograph showing a cross section of a substrate having an insulating film of the invention formed thereon.

Figure 9 is a graph showing an infrared spectrum of an insulating film of the invention for determining water absorption.

Figure 10 is a scanning electron micrograph showing a cross section of a substrate having an insulating film of the invention formed thereon.

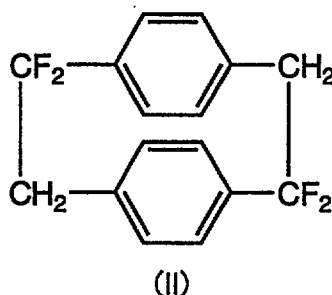
DETAILED DESCRIPTION OF THE INVENTION

The insulating film of the invention consists essentially of poly- α,α -difluoroparaxylylene represented by the following structural formula (I):



In the structural formula (I), n represents a polymerization degree. The polymerization degree n of the poly- α,α -difluoroparaxylylene used in the invention is generally 1,000 or more, and particularly 5,000 or more.

The poly- α,α -difluoroparaxylylene can be formed by the CVD (chemical vapor deposition) process using tetrafluoro-[2,2]-paracyclophane represented by the following structural formula (II) as a raw material:



The synthesis of poly- α,α -difluoroparaxylylene represented by the structural formula (I) by the CVD (chemical vapor deposition) process using tetrafluoro-

5 [2,2]-paracyclophane represented by the following structural formula (II) as a raw material has been known as disclosed in Unexamined Published Japanese Patent Application No. 9-25252. However, the publication only discloses the effect in that a coating film can be formed

10 that is excellent in heat resistance and is expected to have good balance in all the physical properties. In the invention, on the other hand, a poly- α,α -difluoroparaxylylene film is produced under various conditions and examined for properties and characteristics,

15 and thus it has been found that the film is suitable as an interlayer insulating film for a semiconductor device.

A constitutional example of a LPCVD apparatus used for formation of an insulating film of the invention is shown in Figure 1. On producing the insulating film,

20 tetrafluoro-[2,2]-paracyclophane in the form of a dimer as a raw material is put in an evaporation chamber 102 through an inlet 101. In the evaporation chamber 102, the raw material is evaporated to be a dimer gas. The evaporation chamber 102, and a decomposition chamber 103 and a sample

25 chamber 104 connected thereto have different vacuum degrees by a turbo molecular pump 110 and a rotary pump 111, and therefore the dimer gas is introduced into the

decomposition chamber 103 and heated by a heater to be a monomer gas, which is then introduced into the sample chamber 104. In the sample chamber 104, a polymerization reaction occurs on the surface of a sample 107 placed on a
 5 susceptor 106, and a polymer is accumulated to form an insulating film. The susceptor 106 can be rotated by a motor 112, and its temperature can be controlled by a cooler 113. The sample 107 is generally a semiconductor wafer. The monomer gas that does not contribute to the
 10 polymerization and accumulation is introduced to a cooling trap 109 through a vacuum conductance valve 108. The cooling trap 109 is cooled by a cooler 114, and the monomer gas is solidified therein and recovered.

In LPCVD apparatus having such a constitution, the
 15 characteristics and the formation rate of the insulating film can be controlled by adjusting the opening ratio of a shutter 105 for exhaust adjustment provided between the sample chamber 104 and the decomposition chamber 103, the opening ratio of the vacuum conductance valve 108, and the
 20 rotation number and the temperature of the susceptor 106.

In the invention, the conditions for accumulation of the insulating film are preferably controlled to the following ranges:

Heating temperature in the evaporation chamber 102:	
25	80 to 180°C
Heating temperature in the decomposition chamber 103:	
	600 to 750°C
Pressure on accumulation of the insulating film in the sample chamber 104:	
30	1 to 10 Pa, preferably 3 to 6 Pa
Rotation number of the susceptor 106:	
	0 to 10 rpm

Temperature of the susceptor 106:

-60 to 60°C,

preferably -60 to 0°C,

more preferably -60 to -20°C

5 When the temperature of the susceptor 106 (temperature of the substrate) is low, it is preferred since the growing rate of the film is high, the film is liable to be dense, and the yield is improved. The pressure on accumulation of the insulating film in the sample chamber 104 is important
10 for forming a dense insulating film. When the pressure is too high, it is difficult to form a dense insulating film. On the other hand, when it is too low, the growing rate of the film becomes low, and the productivity is deteriorated.

15 By controlling the accumulation conditions to the above-described ranges, characteristics suitable as an interlayer insulating film for a semiconductor device as shown in the following (1) to (7) can be obtained:

- 20 (1) The dielectric constant can be in the range of from 2.1 to 2.7. The dielectric constant of a silicon oxide insulating film is generally 3.9, and the dielectric constant of a silicon oxide insulating film containing fluorine is generally from 3.3 to 3.6.
- 25 (2) A strong adhesive power to a metallic conductive layer, an inorganic insulating layer and a semiconductor substrate can be realized.
- (3) The shape of the insulating film can be worked by ashing by oxygen plasma irradiation.
- (4) The step coverage can be in the range of from 0.4 to 0.9.
- 30 (5) Good gap fill property can be obtained.
- (6) Water absorption can be lowered.

(7) A damascene process on the production of a semiconductor device can be applied.

The above-described characteristics are described in more detail.

5 As described in item (1), the dielectric constant of the insulating film of the invention can be low. Thus, when it is applied for an interlayer insulating film of a semiconductor device having a fine circuit pattern, the capacitance is lowered, and high-speed and normal operation
10 can be ensured. Specifically, it is suitable as an interlayer insulating film in a device of a wiring design rule of a minimum line width of 1 μm or less.

 As described in item (3), the insulating film of the invention can be removed by ashing by oxygen plasma
15 irradiation. Specifically, because sufficient selectivity can be ensured between a resist mask and a hard mask on the oxygen plasma ashing, the insulating film can be easily patterned by ashing.

 The calculation method of the step coverage in item
20 (4) is explained with reference to Figure 2. Figure 2 shows a state in that an insulating film 3 is accumulated on a substrate 1 having a step structure. The step coverage is expressed by B/A , where A represents the thickness of the insulating film 3 at the upper surface of the step, and B represents the minimum thickness of the
25 insulating film 3 at the edge part of the step.

 The gap fill property shown in item (5) shows the capability of filling in a gap, such as a groove and a hole present between electrode layers. When the aspect ratio of
30 the gap becomes high, it is generally difficult to fill the insulating film in the gap without forming any defect such as voids or pinholes. Therefore, the insulating film that

can be filled in a gap having a high aspect ratio is excellent in gap fill property. The aspect ratio is expressed by D/L , where D represents the depth of the gap, and L represents the opening width of the gap. When the gap is in the form of a hole, the opening width L means its via-hole diameter (short diameter). The insulating film of the invention has high gap fill property due to high flowability on film formation, and can be filled with substantially no defect, for example, in a gap having a D/L of 1 or more. Furthermore, it can be easily filled in a gap having a high aspect ratio of from 3 to 10. It can be applied to a fine wiring pattern where L is $0.25\text{ }\mu\text{m}$ or less, and also can be applied to an extremely fine wiring pattern where L is from 0.1 to $0.18\text{ }\mu\text{m}$.

Since the insulating film of the invention is excellent in step coverage and gap fill property, an insulating film having a uniform thickness with no voids can be formed even in a step part and an uneven part having a narrow opening and a high aspect ratio. The insulating film excellent in gap fill property is advantageous on embedding of a capacitance between capacitor electrodes and flattening of various steps in a semiconductor device.

Because the insulating film of the invention has an extremely low water absorption as shown in item (6), it substantially does not adsorb water when it is allowed to stand in the air after formation. Since the insulating film immediately after forming by the CVD process is soft, it is generally hardened by annealing, and water absorption after annealing is also extremely low. Accordingly, the water absorption does not change by heat history. The annealing is generally conducted by heating at a

temperature range of from 300 to 500°C for from 5 to 60 minutes.

The process of the damascene process shown in item (7) is explained with reference to Figures 3A, 3B and 3C. As shown in Figure 3A, a conductive layer (first wiring layer) 21 is formed on a substrate 1, and an insulating film 3 as an interlayer insulating film is formed. The insulating film 3 is etched by the photolithographic process to form a groove 30a in which a second wiring layer is filled, and a via hole 30b in which a conductive material connecting the first wiring layer and the second wiring layer is filled. As shown in Figure 3B, a conductive layer 22 is formed on the insulating film 3 by sputtering or electrolytic plating. At this time, the conductive material is filled in the groove 31a and the via hole 30b. As shown in Figure 3C, the conductive layer 22 is etched by chemical mechanical polishing or reverse sputtering to remove the part present on the insulating film 3, so as to obtain the state where a second wiring layer 22a and a via conductive material 22b are embedded in the insulating film 3. Thus, the damascene process can be applied to the insulating film of the invention. This means that a metallic wiring can be embedded by a photolithographic process, and the insulating film 3 functions as a stopper when the conductive layer 22 is etched by chemical mechanical polishing or reverse sputtering.

A constitutional example of an embodiment in which the insulating film of the invention is used as an interlayer insulating film of a semiconductor device is shown in Figure 4. In Figure 4, a conductive layer (first wiring layer) 21, an insulating film 3 and a conductive layer (second wiring layer) 22 are formed on a substrate 1 in

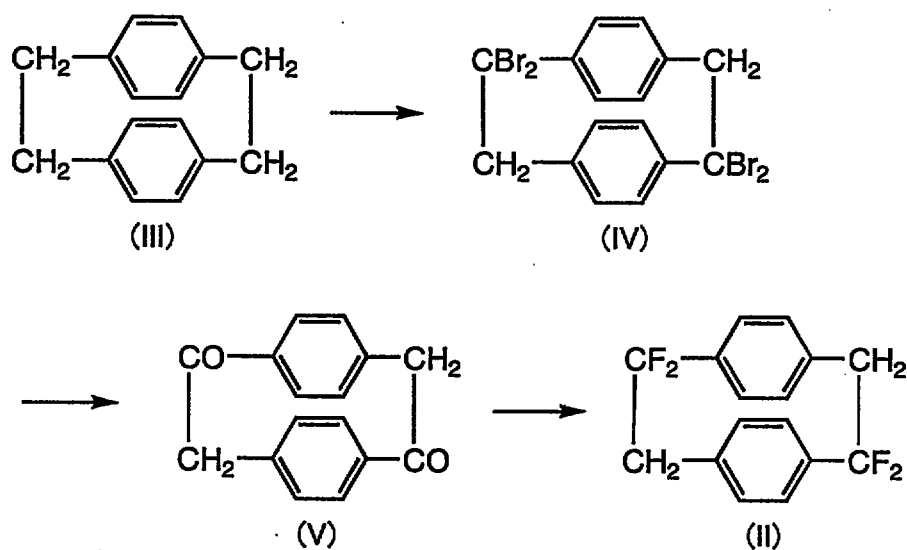
this order, and the conductive layer 21 and the conductive layer 22 are electrically connected by a via conductive material 22b filled in a contact hole piercing the insulating film 3. The insulating film 3 is an interlayer
5 insulating film, and, in the embodiment shown in Figure 4, has a constitution in that inorganic insulating films 3a and 3b are accumulated as sandwiching an insulating film 31 of the invention. The inorganic insulating films 3a and 3b also has functions as a mask for pattern forming, a
10 reinforcing layer for adhesiveness and an anti-hygroscopic film, and generally comprise silicon oxide or silicon nitride. The conductive layer 21 in contact with the substrate 1 generally comprises Al, and the conductive layer 22 not in contact with the substrate 1 generally
15 comprises Cu, Al-Cu or Al-Si-Cu. The via conductive material 22b generally comprises W or Cu since it must have gap fill property. The thickness of the conductive layers 21 and 22 is about from 50 to 500 nm, that of the inorganic insulating films 3a and 3b is about from 50 to 200 nm, and
20 that of the insulating film 31 of the invention is about from 200 to 500 nm. The diameter of the via conductive material 22b is generally from 100 to 500 nm.

In an interlayer insulating film using SOG (spin on glass), a laminated structure where an SOG film is
25 sandwiched by inorganic insulating films has been known. However, since the SOG film absorbs moisture in the SOG laminated structure, moisture is released from the SOG film when wiring (via conductive material) is formed in the adjacent via hole. Due to such moisture release, W absorbs
30 moisture, and conductive failure sometimes occurs. On the other hand, because the insulating film of the invention is

extremely low in water absorption, such conductive failure is difficult to occur.

In the constitutional example shown in Figure 4, while the conductive layers (wiring layers) has a 2-layer structure, the insulating film of the invention can be applied to a constitution having 3 or more conductive layers. The inorganic insulating films 3a and 3b are not necessary and can be provided depending on necessity.

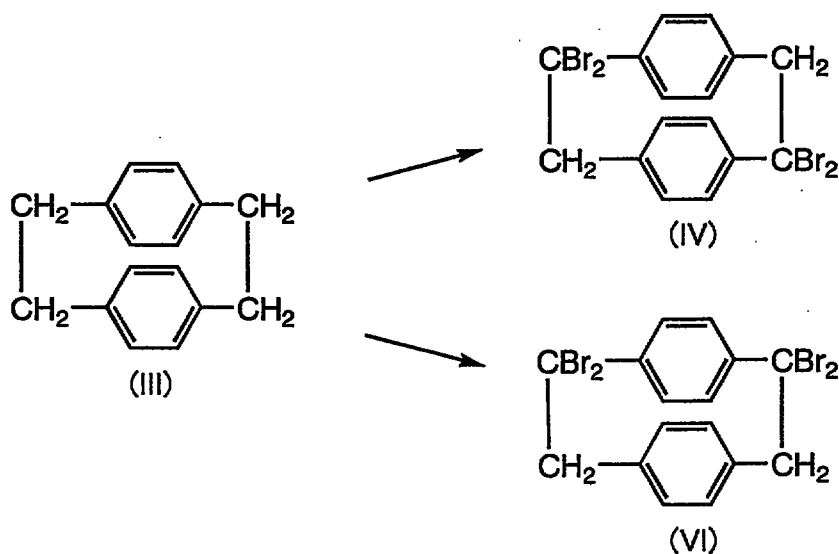
The production process of tetrafluoro-[2,2]-paracyclophane represented by the structural formula (II) used on forming the insulating film of the invention by the CVD process is not particularly limited, and it can be synthesized according to the following route as shown in Unexamined Published Japanese Patent Application No. 9-25252.



[2,2]-Paracyclophane represented by the structural formula (III) used as a starting raw material in this synthesis route is available from Daisan Kasei Co., Ltd. The starting raw material is reacted with N-bromosuccinic

imide in an inert solvent in the presence of a peroxide catalyst, under irradiation of an ultraviolet ray, or under the combination use of a peroxide catalyst and ultraviolet ray irradiation, to obtain tetrabromo-[2,2]-paracyclophane represented by the structural formula (IV). Diketone-[2,2]-paracyclophane represented by the structural formula (V) is obtained by reacting tetrabromo-[2,2]-paracyclophane represented by the structural formula (IV) with sodium acetate or silver acetate in an acetic acid solvent. By reacting diketone-[2,2]-paracyclophane represented by the structural formula (V) with a fluorination agent such as tetrafluoro sulfur and diethylaminosulfur trifluoride (DAST), tetrafluoro-[2,2]-paracyclophane represented by the structural formula (II) as the objective compound can be obtained.

On the reaction obtaining tetrabromo-[2,2]-paracyclophane represented by the structural formula (IV) from [2,2]-paracyclophane represented by the structural formula (III), a brominated compound represented by the structural formula (VI) is also formed according to the following scheme:



The brominated compound represented by the structural formula (VI) can be separated by utilizing difference in solubility in the solvent.

5

EXAMPLE

EXAMPLE 1

The insulating film of the invention was produced and its dielectric constant was measured.

10 Tetrafluoro-[2,2]-paracyclophane represented by the structural formula (II) used as a raw material of the CVD process was produced according to the method described in Unexamined Published Japanese Patent Application No. 9-25252.

15 Poly- α,α -difluoroparaxylylene represented by the structural formula (I) was accumulated on a substrate having a flat surface by using a vacuum CVD apparatus having a constitution shown in Figure 1. The conditions of accumulation were as follows:

Heating temperature in the evaporation chamber 102:

20 120°C

Heating temperature in the decomposition chamber 103:

700°C

Pressure on accumulation of the insulating film in the sample chamber 104:

25 4 Pa

Temperature of the susceptor:

-40°C

The accumulation time was 30 minutes. After accumulation, annealing was conducted at 350°C for 30
30 minutes. As a substrate, a copper substrate and a p-type semiconductor Si wafer were used. After forming an insulating film having a thickness of 1 μm on the

substrates, an Al electrode was continuously formed by sputtering, to obtain samples for measurement.

The samples for measurement were subjected to measurement of capacitance between the Al electrode and the copper substrate or between the Al electrode and the p-type semiconductor Si wafer with a 1-MHz C-V plotter. As a result, the dielectric constant of the insulating film was in the range of from 2.1 to 2.7.

EXAMPLE 2

The adhesive power of the insulating film was measured. By using an Si wafer as a substrate, an insulating film (thickness: 220 nm) of the invention was formed and annealed under the same conditions as in Example 1. An adhesive tape was adhered on the insulating film and then peeled off, but the insulating film was not peeled.

EXAMPLE 3

The oxygen plasma ashing was conducted on the insulating film.

An insulating film (thickness: 560 nm) of the invention was formed on an Si wafer under the same conditions as in Example 1, and after accumulation, annealing was conducted at 350°C for 75 minutes. After a mask was formed by photoresist, it was placed on a substrate stage of a plasma asher, and oxygen plasma ashing was conducted under the following conditions:

Oxygen gas flow amount:	90 SCCM
Vacuum degree:	8 Pa
RF power:	4.1 Watt/cm ² (13.56 MHz)
Ashing rate:	113.3 nm/min

After ashing, the insulating film was removed according to the mask pattern, and burning flaw was not observed on the insulating film after ashing.

EXAMPLE 4

The step coverage and the gap fill property of the insulating film were measured.

5 An insulating film (thickness: 250 nm) of the invention was formed on an Si wafer having a via hole having an opening diameter of 0.18 μm and an aspect ratio of 8, to fill the insulating film in the via hole. The conditions for accumulation of the insulating film were the same as in Example 1. After forming the insulating film, 10 the substrate was cut at a face perpendicular to the main plane of the substrate. Al was deposited on the cut surface, which was then observed by a scanning electron microscope. A scanning electron micrograph thus obtained is shown in Figure 5, and an enlarged view thereof is shown 15 in Figure 6. In Figures 5 and 6, a part having a high brightness is the insulating film. It is understood from these figures that the insulating film of the invention is filled in the via hole having a small opening diameter and a large aspect ratio without voids.

20 The insulating film of the invention was formed on a substrate having a surface of a step structure containing complicated unevenness. The conditions for accumulation of the insulating film were the same as in Example 1. Scanning electron micrographs after the formation of the 25 insulating film are shown in Figures 7 and 8. It is understood from these figures that in the insulating film, a bridge connecting protrusions of the unevenness is not observed, and the formation of voids is not observed.

EXAMPLE 5

30 Water absorption of the insulating film was measured.

The insulating film (thickness: 220 nm) of the invention was formed on an Si substrate under the same

conditions as in Example 1. The resulting samples for measurement were allowed to stand in the air (23°C, 65%RH) for 48 hours. They were then annealed in an electric furnace in a nitrogen atmosphere for 30 minutes. The
5 annealing temperature was 300°C, 350°C or 400°C. They were then further allowed to stand in the air for 48 hours. A part of samples was not subjected to the annealing but continuously allowed to stand in the air for 96 hours.

The insulating film of the samples was measured for
10 infrared spectrum to determine the change in water absorption. The results are shown in Figure 9. The heat history corresponding to the spectra S1 to S4 is as follows:

- S1: Continuously allowed to stand in the air
- 15 S2: Annealing temperature of 300°C
- S3: Annealing temperature of 350°C
- S4: Annealing temperature of 400°C

The spectrum S5 is for an aluminum base of an infrared spectroscope.

20 It is understood from Figure 9 that change in wave shape of an OH group (appearing near 3,300 cm⁻¹) due to water absorption is not observed in all the insulating films having any heat history. Accordingly, the insulating film of the invention exhibits substantially no water
25 absorption immediately after the film formation and after suffering heat history by annealing.

EXAMPLE 6

The insulating film of the invention was applied to the damascene process.

30 An insulating film (thickness: 350 nm) of the invention was formed on an Si wafer under the same conditions as in Example 1, and subjected to annealing

under the same conditions as in Example 1. After forming a via hole in the insulating film, a Cu conductive layer was formed on the insulating film by sputtering. The diameter of the via hole was 0.25 μm . The Cu conductive layer was
5 then etched by chemical mechanical polishing. As a result, the polishing was stopped at the surface of the insulating film, and a state, in which a copper plug having a flat surface was filled in the via hole of the insulating film, was obtained. The scanning electron micrograph after
10 polishing is shown in Figure 10.

In the present invention, poly- α,α -difluoroparaxylylene is applied to an interlayer insulating film of a semiconductor device. Accordingly, the capacitance coupling is lowered, and high-speed and normal
15 operation can be ensured in a semiconductor device having a fine circuit pattern.



What is claimed is:

1. An insulating film for a semiconductor device used as an interlayer insulating film of a semiconductor device, said insulating film consisting essentially of
5 poly- α,α -difluoroparaxylylene and having a relative dielectric constant of from 2.1 to 2.7.
2. An insulating film for a semiconductor device used as an interlayer insulating film of a semiconductor device, said insulating film consisting essentially of
10 poly- α,α -difluoroparaxylylene and exhibiting a step coverage of from 0.4 to 0.9.
3. An insulating film for a semiconductor device capable of being filled in a gap, said insulating film consisting essentially of poly- α,α -difluoroparaxylylene,
15 having a ratio (D/L) of a depth (D) and an opening width (L) of 1 or more.
4. An insulating film for a semiconductor device as claimed in one of claims 1 to 3, wherein a shape of said insulating film is capable of being patterned by
20 irradiation of oxygen plasma.
5. A semiconductor device comprising a semiconductor substrate having thereon at least two conductive layers through an interlayer insulating film, said interlayer insulating film is an insulating film as claimed in one of
25 claims 1 to 4.