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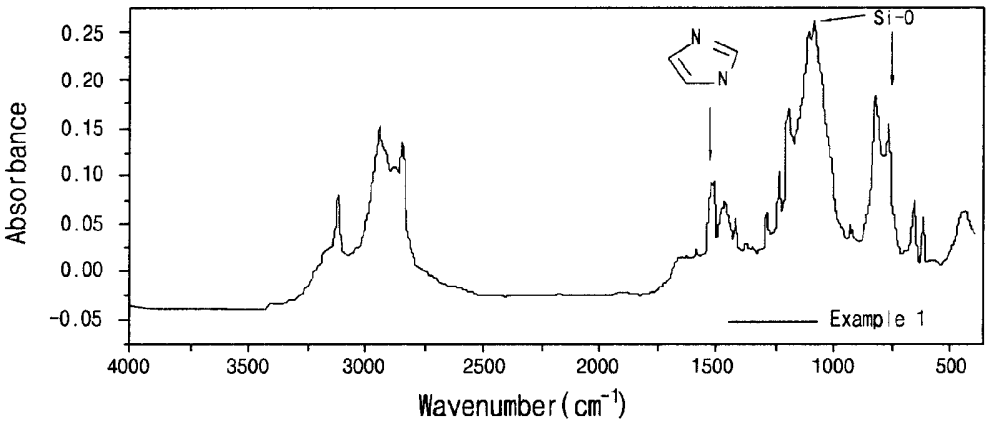

(57) Abstract: Disclosed is a method of surface modifying a polyimide film, a method of manufacturing a flexible copper clad laminate using the same, and a flexible copper clad laminate having a two-layer structure manufactured thereby. The method of surface modifying a polyimide film of the current invention includes first-treating the surface of the polyimide film with plasma, dipping the polyimide film into a solution containing a silane coupling agent, which is prepared by adding 1 mol of a compound represented by Formula 1 with 0.25~1 mol of a compound represented by Formula 2, to surface treat the polyimide film, and second-treating the surface of the polyimide film with plasma, and therefore, may simplify conventional methods of surface modifying a polyimide film. In addition, since the flexible copper clad laminate of the current invention, which has a two-layer structure formed through copper sputtering and electroplating on the modified polyimide film, has excellent adhesive strength between the polyimide film and the copper foil, it may be usefully applied to electronic parts, such as flexible printed circuit boards, TCPs (Tape Carrier Packages), COFs (Chips On Film), etc.

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【DESCRIPTION】

【Invention Title】

METHOD OF SURFACE MODIFICATION OF POLYIMIDE FILM USING SILANES COUPLING AGENT, MANUFACTURING METHOD OF FLEXIBLE COPPER CLAD LAMINATE AND ITS PRODUCT THEREBY

【Technical Field】

The present invention relates to a method of surface modifying a polyimide film, a method of manufacturing a flexible copper clad laminate (FCCL) using the same, and an FCCL having a two-layer structure manufactured thereby. More particularly, the present invention relates to a method of surface modifying a polyimide film, comprising first-treating a polyimide film with plasma, dipping the polyimide film into a solution containing a silane coupling agent for surface treatment, and then second-treating the polyimide film with plasma to surface modify the polyimide film, to a method of manufacturing a polyimide FCCL having a two-layer structure using the method of modifying surface of a polyimide film, and to a polyimide FCCL having excellent adhesive strength manufactured using the manufacturing method.

【Background Art】

A polyimide film has heat resistance, electrical properties, chemical resistance and bending resistance that are superior to other polymer materials, and thus may be variously used as insulating substrate material for electronic parts, such as flexible printed circuit boards, tape automated bonding (TAB), COFs (Chips On Film), etc. A conventional CCL used in a flexible printed circuit board is exemplified by a CCL having a three-layer structure using an epoxy adhesive. However, CCL has deteriorated dimensional stability because heat resistance of the adhesive is poor. Hence, the conventional CCL has been deemed unsuitable for fine patterning. Recently, thorough attempts have been made to replace a conventional product having a three-layer structure with a product having a two-layer structure. The two-layer structure is realized by directly die-casting a polyimide film to a copper foil or bonding a polyimide film to a copper foil at a high temperature without the need for an adhesive layer, and therefore, provides advantages such as easy formation of fine patterns and high flexibility. Moreover, by virtue of the above-mentioned advantages, a CCL having a two-layer structure may be more widely marketable for use in display products, such as folding mobile phones, LCDs, PDP modules, etc. In particular, since Korea mainly imports substrate materials for use in electronic parts, the

development of an FCCL having a two-layer structure using a novel process has been urgently required.

It has been reported on method of manufacturing a two-layered FCCL that was manufactured by laminating a polyimide film and a copper foil, rather than using an adhesive. In addition, sputtering-electroplating methods have been proposed, in which a thin metal seed layer (nickel, chromium, etc.) is formed through sputtering, and then a copper layer is formed to a desired thickness through electroplating thereon. However, the above method suffers because the surface modification of the polyimide film should be preceded using plasma or ion beams, during which a specific seed layer is needed. Particularly, when both-sided copper clad laminate is manufactured, specific equipment is needed, thus the manufacturing cost becomes increased. Further, since the adhesive strength of the CCL becomes unstable under conditions of high temperature and high humidity, reliability is decreased. Furthermore, a drilling process, which is conducted after a printed circuit board is manufactured, may cause environmental contamination.

Leading to the present invention, intensive and thorough effort to obtain an FCCL having a two-layer structure, carried out by the present inventors, aiming to avoid the problems encountered in the related art, led to the

development of a method of manufacturing an FCCL having a two-layer structure, which comprises modifying surface of a polyimide film through first plasma treatment, dipping into a solution containing a silane coupling agent for surface treatment and then second plasma treatment, and sequentially copper sputtering and electroplating the surface modified polyimide film under optimal conditions, thus the resultant FCCL can have excellent adhesive strength between the film and a copper foil and can maintain adhesive strength at high temperatures for a long period of time.

【Disclosure】

【Technical Problem】

An object of the present invention is to provide a method of surface modifying a polyimide film.

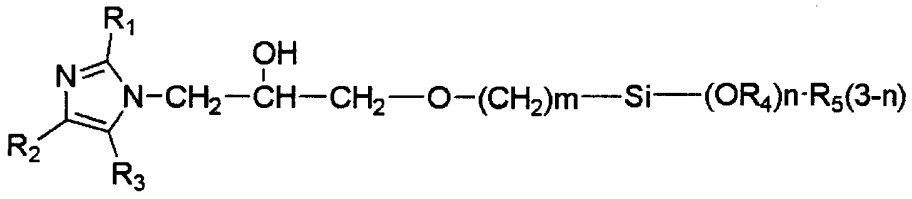
Another object of the present invention is to provide a method of manufacturing an FCCL having a two-layer structure using the method of surface modifying a polyimide film.

A further object of the present invention is to provide an FCCL having a two-layer structure on either or both surfaces of the polyimide film, manufactured using the above manufacturing method.

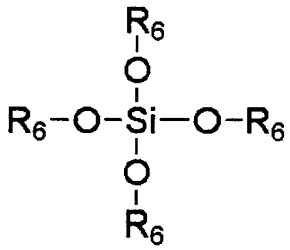
【Technical Solution】

In order to achieve the above objects, the present invention provides a method of surface modifying a polyimide film, comprising 1) modifying surface of a polyimide film through first plasma treatment; 2) dipping the polyimide film into a solution containing a silane coupling agent, which is prepared by mixing a compound represented by Formula 1 below and a compound represented by Formula 2 below with mole ratio 1: 0.25~1 to treat the surface thereof; and 3) modifying surface of the polyimide film through second plasma treatment:

Formula 1



Formula 2



in Formulas 1 and 2, R_1, R_2 and R_3 are each hydrogen or a C_1~C_{10} alkyl group or vinyl group, R_4 and R_5 are each -$(CH_2)x$-, x is 1~4, R_6 is a C_1~C_5 alkyl group, aryl group or cyano group, m is 1~5 and n is 1~3.

In the above method, the solution containing the silane coupling agent means that the solution contains 0.01~10 wt% of a silane coupling agent, into which the polyimide film is dipped for 1~60 min. Further, the solution containing the silane coupling agent is prepared by dissolving a silane coupling agent in at least one solvent selected from the group consisting of water, acetone, methanol, ethanol, and isopropanol.

The plasma treatment is conducted at 20~100 W under pressure in a vacuum chamber of $1x10^{-3}$~$1x10^{-5}$ torr for 10~1,000 sec using a direct current (DC) or 60 Hz high-frequency power source.

In addition, the present invention provides a method of manufacturing an FCCL using the method of surface modifying a polyimide film. Specifically, the method comprises copper sputtering either or both surfaces of the modified polyimide film at 0.5~30 mA and 50~500 W for 1~10 hours, to form a copper sputtering layer, which is then electroplated to form a copper electroplating layer.

The copper sputtering layer has thickness of 500~5,000 Å, and the copper electroplating layer has thickness of 1~50 ㎛.

In addition, the present invention provides a polyimide FCCL having a two-layer structure, which comprises a 500~5,000 Å thick copper sputtering layer formed on either surface of the polyimide film prepared using the above surface modification method, and a 1~50 ㎛ thick copper electroplating layer formed on the copper sputtering layer.

In addition, the present invention provides a polyimide FCCL having a two-layer structure, which comprises a 500~5,000 Å thick copper sputtering layer formed on each of both surfaces of the polyimide film prepared using the surface modification method, and a 1~50 ㎛ thick copper electroplating layer formed on the copper sputtering layer.

【Advantageous Effects】

According to the present invention, the polyimide film is subjected to a surface modification process including first plasma treatment, surface treatment through dipping in a solution containing silane coupling agent and then second plasma treatment to modify the surface thereof. Thus, the above process is advantageous because it may substitute for a conventional surface treatment process using ion beams

without the need for a specific seed layer, therefore decreasing the cost and reducing environmental contamination due to the use of heavy metals.

In addition, a polyimide FCCL having a two-layer structure is provided, and, in particular, a single-sided or double-sided polyimide FCCL may be provided by surface modifying either or both surfaces of the polyimide film.

【Description of Drawings】

FIG. 1 is an FT-IR spectrum of a silane coupling agent used in Example 1 of the present invention;

FIG. 2 is a scanning electron micrograph (SEM) of a polyimide film of Example 1 of the present invention;

FIG. 3 is an SEM of a polyimide film of Comparative Example 1 of the present invention;

FIG. 4 is an SEM of a polyimide film of Comparative Example 2 of the present invention;

FIG. 5 is an SEM of a polyimide film of Comparative Example 3 of the present invention;

FIG. 6 is an AFM (Atomic Force Microscopy) image of the polyimide film of Example 1 of the present invention;

FIG. 7 is an AFM image of the polyimide film of Comparative Example 1 of the present invention;

FIG. 8 is an AFM image of the polyimide film of Comparative Example 2 of the present invention;

FIG. 9 is an AFM image of the polyimide film of Comparative Example 3 of the present invention;

FIG. 10 is a result of an ESCA (Electron Spectroscopy of Chemical Analysis) of the polyimide film of the present invention;

FIG. 11 is a schematic view of a plasma device used in the present invention; and

FIG. 12 is a schematic view of a pulse DC sputtering device used in the present invention.

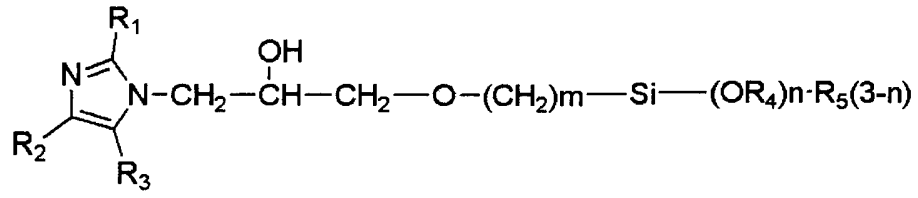
【Best Mode】

Hereinafter, a detailed description will be given of the present invention.

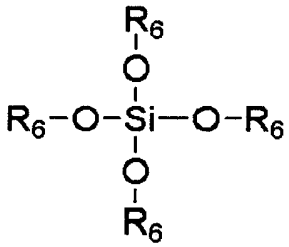
In order to provide a polyimide FCCL having improved adhesive strength, the present invention provides a method of surface modifying a polyimide film, which comprises 1) modifying surface of a polyimide film through first plasma treatment; 2) dipping the polyimide film into a solution containing a silane coupling agent, which is prepared by mixing a compound represented by Formula 1 below and a compound represented by Formula 2 below with mole ratio 1:

0.25~1 to treat the surface thereof; and 3) modifying surface of the polyimide film through second plasma treatment:

Formula 1



Formula 2



in Formulas 1 and 2, R_1, R_2, R_3, R_4, R_5, R_6, m and n are defined as above.

Examples of the polyimide film usable in the present invention include, but are not limited to, synthetic or commercially available ones, as long as the polyimide film may be 10~100 ㎛ thick. Preferably, the polyimide film is exemplified by Kapton H or Kapton E, available from Dupont

Co. Ltd., USA, Upilex-S, available from Ube Co. Ltd., Japan, or Apical film, available from Kaneka Co. Ltd., Japan.

As for the surface modification method of the polyimide film, the first plasma treatment in the first step is a process of supplying a hydrophilic group to the surface of the polyimide film. The plasma treatment is preferably conducted using argon gas, oxygen gas or nitrogen gas alone, or a gas mixture of argon and oxygen, of argon and nitrogen or of nitrogen and oxygen mixed at an appropriate ratio. The appropriate ratio of the gas mixture is 0.5~5 cc/min.

The plasma treatment is carried out at 20~100 W under pressure in a vacuum chamber of $1x10^{-3}$~$1x10^{-5}$ torr for 10~1000 sec using a DC or 60 Hz high-frequency power source. When the polyimide film is treated with plasma at a high power for a long period of time in a gas atmosphere including excess oxygen, nitrogen or argon, the surface of the polyimide film may suffer enormous damage, such as carbonization, and thus, the inherent properties of the polyimide film may be deteriorated. Consequently, it is impossible to use the polyimide film as the insulating material of a substrate.

As for the surface modification method of the polyimide film, the dipping of the polyimide film into the solution containing a silane coupling agent for surface treatment in the second step functions to induce a graft

reaction between the hydrophilic group supplied to the surface of the polyimide film through the first plasma treatment and the solution containing a silane coupling agent, in order to assure high adhesive strength between the polyimide film and a copper foil to be subsequently formed.

The silane coupling agent of the present invention is prepared by reacting a mixture comprising an imidazole derivative and organosilne-based epoxy mixed at equal amounts at 50~150℃ for 60 min in a nitrogen atmosphere to prepare a compound of Formula 1, adding 1 mol of the compound of Formula 1 with 0.25~1 mol of a compound of Formula 2, allowing them to react at 150~200℃ for 1~5 hours, and then removing undesirably produced methanol under reduced pressure.

FIG. 1 is an FT-IR spectrum of the siliane coupling agent used in Example 1 of the present invention. As is apparent from this result, the silane coupling agent of the present invention is confirmed to have imidazole and silane functional groups.

The solution containing a silane coupling agent of the present invention is a solution containing 0.01~10 wt% of silane coupling agent, into which the polyimide film is then dipped for 1~60 min. As such, a solvent usable upon the preparation of the solution containing a silane coupling

agent is not particularly limited, but preferably includes at least one selected from the group consisting of water, acetone, methanol, ethanol, and isopropanol, each of which has a low boiling point.

The coupling agent is dissolved to 0.01~10 wt% in an organic solvent or water or a solvent mixture comprising organic solvent and water, to prepare a desired dipping solution, into which the polyimide film is then dipped. The dipping process is preferably conducted for 1~60 min. A dipping time shorter than 1 min results in an insufficiently induced reaction of the silane coupling agent. In contrast, when the dipping time exceeds 60 min, adhesive strength and heat resistance are not further increased in proportion to the reaction time.

FIGS. 2 to 5 are SEMs showing the surfaces of the polyimide films prepared in Example 1 and Comparative Examples 1 to 3. FIG. 2 illustrates the surface of the polyimide film of Example 1, FIG. 3 illustrates the surface of the polyimide film of Comparative Example 1, FIG. 4 illustrates the surface of the polyimide film of Comparative Example 2, and FIG. 5 illustrates the surface of the polyimide film of Comparative Example 3. From the results shown in these drawings, the polyimide film of Example 1,

surface treated using the method of the present invention, can be seen to have a concavo-convex pattern.

FIGS. 6 to 9 are AFM images showing the surfaces of the polyimide films prepared in Example 1 and Comparative Examples 1 to 3. FIG. 6 illustrates the surface of the polyimide film of Example 1, FIG. 7 illustrates the surface of the polyimide film of Comparative Example 1, FIG. 8 illustrates the surface of the polyimide film of Comparative Example 2, and FIG. 9 illustrates the surface of the polyimide film of Comparative Example 3. From the results shown in these drawings, the polyimide film of Example 1, surface treated using the method of the present invention, can be seen to have very small protrusions formed thereon.

FIG. 10 illustrates the result of ESCA of the polyimide film of the present invention. From this result, the polyimide film of Example 1, treated using the surface modification method of the present invention, can be confirmed to have high hydrophilicity by virtue of very high oxygen content.

After the dipping process at 50~100℃ for 1~60 min, the surface modified polyimide film is washed with distilled water and alcohol to remove an unreacted solution, the

surface of which is then sufficiently dried in an oven at 100℃ or less for a subsequent process.

As for the surface modification method of the polyimide film of the present invention, the second plasma treatment in the third step is conducted by supplying an oxygen functional group to the surface of the polyimide film such that a higher hydrophilic group is provided to the surface of the polyimide film having low hydrophilicity.

In this case, the second plasma treatment is conducted in the same manner as in the first plasma treatment.

FIG. 11 schematically illustrates a plasma device 10 of the present invention. While a polyimide film 3 is wound on rollers 4, argon gas, oxygen gas or a gas mixture of argon and oxygen is supplied in an amount of 5~30 sccm into a vacuum chamber 2 maintained to $1x10^{-3}$~$1x10^{-5}$ torr through inlets 1, 5 thereof to form a plasma treatment atmosphere. Subsequently, plasma treatment is conducted using plasma sources 6, 8 disposed at upper and lower portions of the vacuum chamber 2 under conditions of current of 1~100 mA and volatge of 0.25~10 KV.

In addition, the present invention provides a method of manufacturing an FCCL using the surface modification method of the polyimide film. Specifically, the manufacturing method of the present invention comprises

1) modifying the surface of a polyimide film using a surface modification process of a polyimide film;

2) copper sputtering either or both surfaces of the polyimide film dried in the previous step at 0.5~30 mA and 50~500 W for 1~10 hours to form a copper sputtering layer; and

3) electroplating the copper sputtering layer to form a copper electroplating layer.

In the first step, the surface modification process of the polyimide film used in the present step is mentioned as above, in which the polyimide film is first-treated with plasma to supply a hydrophilic group to the surface thereof, dipped into the solution containing a silane coupling agent for surface treatment to induce a graft reaction so as to increase the adhesive strength between the polyimide film and the copper foil, and is then second-treated with plasma to supply the oxygen functional group to the surface thereof, thereby realizing higher hydrophilicity.

In the second step, the surface modified polyimide film is sputtered by colliding with copper to form a copper foil. The sputtering process is conducted using a pulse DC sputtering device 20 depicted in FIG. 12. The polyimide film 13 surface modified in the previous step is wound on rollers 14, and argon gas is supplied in an amount of 5~30 sccm into

a vacuum chamber 12 maintained to $1x10^{-3}$~$1x10^{-5}$ torr through an inlet 11 thereof to form a sputtering atmosphere. Thereafter, while current of 0.5~30 mA is controlled with power of 50~500 W, copper sputtering is conducted for 1~10 hours, thus forming a copper sputtering layer having a thickness of 500~5,000 Å. If the copper sputtering layer is thinner than 500 Å, pinholes may be formed or current does not flow upon electroplating. Further, this layer may peel due to its low plating adhesion. On the other hand, if the copper sputtering layer is thicker than 5,000 Å, energy loss is large and the layer is too thick to be suitable for use in substrate.

In the third step, the polyimide film having the copper sputtering layer is loaded into an electroplating bath including copper sulfate and an aqueous sulfuric acid solution, and thus a thin copper electroplating layer is formed on the copper sputtering layer of the polyimide film, thereby manufacturing a CCL. As such, the copper foil is preferably 1~50 ㎛ thick. When the copper electroplating layer, that is, the copper foil, is thinner than 1 ㎛, the CCL may have pinholes formed therein and be difficult to handle. On the other hand, when the copper foil is thicker than 50 ㎛, the line/space accuracy of highly dense wires may

be decreased. Further, part mounting ability is undesirably reduced in terms of light weight and miniaturization.

In addition, the present invention provides a polyimide FCCL having a two-layer structure manufactured using the above manufacturing method of the present invention. The polyimide FCCL having a two-layer structure of the present invention is comprising a 500~5000 Å thick copper sputtering layer on either surface of the polyimide film modified using the method of the present invention and a 1~50 ㎛ thick copper electroplating layer on the copper sputtering layer.

Moreover, both surfaces of polyimide film modified using the surface modification method of the present invention may be subjected to the above processes, thereby providing a double-sided polyimide FCCL having a two-layer structure.

The polyimide FCCL of the present invention has adhesive strength of 0.8 kg/cm or more between the polyimide film and the copper foil, and in particular, can maintain adhesive strength of 0.7 kg/cm or more even under deterioration conditions of 150℃ for one week or more. Thus, the polyimide FCCL of the present invention can exhibit sufficient adhesive strength even though it is exposed to high temperatures for a long period of time.

The CCL having a two-layer structure of the present invention can be applied to processes of forming a copper circuit pattern by forming a mask having a predetermined pattern and then selectively etching the exposed copper foil using a copper ethant to remove it, and is therefore suitable for use in material for a substrate for electronic parts, such as a flexible printed board, TCP (Tape Carrier Package), COF (Chip On Film), etc.

【Mode for Invention】

Hereinafter, the present invention is specifically explained using the following examples and comparative examples which are set forth to illustrate, but are not to be construed to limit the present invention.

<Example 1>

Step 1: Preparation of Silane Coupling Agent

1 mol of 1-imidazole was reacted with 1 mol of 3-glycidoxy propyltrimethoxysilane at 100℃ for 60 min in a nitrogen atmosphere to prepare a compound of Formula 1. Subsequently, 1 mol of the compound of Formula 1 thus prepared was added with 1 mol of tetramethyl orthosilicate as a compound of Formula 2, followed by allowing them to react at 120℃ for 2 hours. After the reaction, undesirably

produced methanol was removed under reduced pressure, thus preparing a silane coupling agent.

Step 2: Preparation of Polyimide CCL

A polyimide film (Kapton E, Dupont) was loaded into a chamber of a plasma device and then surface treated for 200 sec using plasma generated at current of 6 mA and voltage of 1 KV under pressure of 3×10^{-3} torr in an argon atmosphere.

The silane coupling agent prepared in Step 1 was dissolved to 1 wt% in a solvent mixture comprising water and methanol mixed at 1:1, to prepare a dipping solution, into which the surface treated polyimide film was then dipped for 20 min and subsequently reacted in an oven at 100℃ for 60 min. Thereafter, the resultant film was washed with methanol and dried in an oven.

The dried film was loaded into the plasma chamber and then subjected to second plasma treatment for 700 sec using plasma generated at 1 KV and 6 mA under 5×10^{-3} torr in an argon atmosphere. Subsequently, the film was loaded into a sputtering device and then sputtered at 3.5 mA and 200 W for 1 hour in a vacuum of 4×10^{-3} torr while controlling the pressure using argon gas. The resultant copper foil had a uniform thickness of 2,500 Å. Then, electroplating was

conducted in an electroplating bath to form a 20 ㎛ thick copper plating layer, thereby manufacturing a polyimide CCL.

<Example 2>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 1, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 2 of Table 1 below, was used, instead of the silane coupling agent of Step 1 of Example 1.

<Example 3>

Instead of the silane coupling agent of Step 1 of Example 1, a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 3 of Table 1 below, was used. The silane coupling agent was dissolved to 0.5 wt% in a solvent mixture comprising water and methanol mixed at 1:1 to prepare a dipping solution, into which the polyimide film (Kapton E, Dupont), surface treated in the same manner as in Step 2 of Example 1, was then dipped for 10 min, reacted in an oven at 100℃ for 1 hour, washed with distilled water and then dried. Thereafter, the polyimide film, modified through second plasma treatment under the same conditions as Example 1, was sputtered with copper to form a 3000 Å thick copper

sputtering layer, which was then electroplated, thus manufacturing a 45 ㎛ thick polyimide CCL.

<Example 4>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 3, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 4 of Table 1 below, was used instead of the silane coupling agent of Step 1 of Example 1, and such a silane coupling agent was dissolved to 0.1 wt% in a solvent mixture comprising water and methanol mixed at 1:1 to prepare a dipping solution.

<Example 5>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 3, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 5 of Table 1 below, was used instead of the silane coupling agent of Step 1 of Example 1, and such a silane coupling agent was dissolved to 0.1 wt% in a solvent mixture comprising water and methanol mixed at 1:1 to prepare a dipping solution.

<Example 6>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 3, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 6 of Table 1 below, was used instead of the silane coupling agent of Step 1 of Example 1, and such a silane coupling agent was dissolved to 0.1 wt% in a solvent mixture comprising water and methanol mixed at 1:1 to prepare a dipping solution.

<Example 7>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 3, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 7 of Table 1 below, was used instead of the silane coupling agent of Step 1 of Example 1, and such a silane coupling agent was dissolved to 0.5 wt% in isopropanol to prepare a dipping solution.

<Example 8>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 1, with the exception that a silane coupling agent, prepared using compounds of Formulas 1 and 2 shown in Example 8 of Table 1 below, was used instead of the silane coupling agent of Step 1 of Example 1, and such a

silane coupling agent was dissolved to 0.1 wt% in ethanol to prepare a dipping solution.

<Example 9>

A 20 ㎛ thick polyimide FCCL was manufactured in the same manner as in Example 1, with the exception that a film (Upilex-S, Ube, Japan) was used instead of the polyimide film of Step 1 of Example 1.

【Table 1】

Silane Coupling Agent

Ex. No.	Formula 1		Formula 2
	Imidazole Derivative (1 mol)	Organosilane-based EpoxyDerivative (1 mol)	
Ex. 1	1-Imidazole	3-Glycidoxy Propyltrimethoxysilane	Tetramethyl Orthosilicate (1 mol)
Ex. 2	1-Imidazole	3-Glycidoxy Propyltrimethoxysilane	Tetramethyl Orthosilicate (0.25 mol)
Ex. 3	2-Methyl-imidazole	3-Glycidoxy Propyltrimethoxysilane	Tetraethyl Orthosilicate (0.5 mol)
Ex. 4	2-Methyl-imidazole	3-Glycidoxy Propyltriethoxysilane	Tetraethyl Orthosilicate (0.5 mol)
Ex. 5	2-Methyl-imidazole	3-Glycidoxy Propyltrimethoxysilane	Tetrapropoxy-silane (0.5 mol)

Ex. 6	2-Ethyl-4-methyl-imidazole	3-Glycidoxy Propylsilane	Tetraisopropoxy-silane (0.5 mol)
Ex. 7	1-Imidazole	3-Glycidoxy Propyltriethoxysilane	Tetramethyl Orthosilicate (0.5 mol)
Ex. 8	1-Imidazole	3-Glycidoxy Propyltrimethoxysilane	Tetramethyl Orthosilicate (1 mol)

<Comparative Example 1>

A polyimide film (Kapton E, Dupont) was copper sputtered and electroplated in the same manner as in Example 1, with omission of a surface modification process includes first plasma treatment, reaction with a coupling agent and second plasma treatment, thus manufacturing a 20 ㎛ thick polyimide CCL.

<Comparative Example 2>

A polyimide film (Kapton E, Dupont) was subjected to first plasma treatment in the same manner as in Example 1, with omission of surface modification using a coupling agent and subsequent second plasma treatment, and was then copper sputtered and electroplated in the same manner as in Example 1, thus manufacturing a 20 ㎛ thick polyimide CCL.

<Comparative Example 3>

A polyimide film (Kapton E, Dupont) was subjected to first plasma treatment in the same manner as in Example 1 and surface modification using the silane coupling agent used in Example 1, with omission of second plasma treatment, and was then copper sputtered and electroplated in the same manner as in Example 1, thus manufacturing a 20 ㎛ thick polyimide CCL.

<Comparative Example 4>

A polyimide film (Kapton E, Dupont) was subjected to first plasma treatment in the same manner as in Example 1 and surface modification using the silane coupling agent used in Example 3, with omission of second plasma treatment, and was then copper sputtered and electroplated in the same manner as in Example 1, thus manufacturing a 20 ㎛ thick polyimide CCL.

<Comparative Example 5>

A polyimide film (Kapton E, Dupont) was subjected to first plasma treatment in the same manner as in Example 1 and surface modification using the silane coupling agent used in Example 7, with omission of second plasma treatment, and was then copper sputtered and electroplated in the same manner as in Example 1, thus manufacturing a 20 ㎛ thick polyimide CCL.

<Experimental Example 1>

The properties of the polyimide CCLs manufactured in the examples and comparative examples were measured as follows.

1. Measurement of Adhesive Strength

The surface of each of the CCLs subjected to electroplating in Examples 1~9 and Comparative Examples 1~5 was patterned using acid resistant paint or acid resistant tape, and was then etched using an etchant comprising sulfuric acid or copper sulfate, after which the 90°peel strength thereof was measured. The results of contact angle and adhesive strength are given in Tables 2 and 3, below.

【Table 2】

Results of Measurement of Contact Angle

Ex. No.	Contact Angle
Comparative Example 1	67.7°
Comparative Example 2	31.2°
Comparative Example 3	62.3°
Example 2	17.5°
Example 4	18.6°
Example 6	18.3°
Example 8	17.9°

【Table 3】

Results of Measurement of Adhesive Strength

Ex. No.	First Plasma Treatment	Treatment with Coupling Agent	Second Plasma Treatment	Adhesive Strength (kg/cm)	Aging Test (150℃ after 7 days) Adhesive Strength (kg/cm)
Ex. 1	Yes	Yes	Yes	1.12	0.84
Ex. 2	Yes	Yes	Yes	0.94	0.77
Ex. 3	Yes	Yes	Yes	0.83	0.80
Ex. 4	Yes	Yes	Yes	0.92	0.90
Ex. 5	Yes	Yes	Yes	0.95	0.88
Ex. 6	Yes	Yes	Yes	1.29	0.99
Ex. 7	Yes	Yes	Yes	1.02	0.86
Ex. 8	Yes	Yes	Yes	1.15	0.95
Ex. 9	Yes	Yes	Yes	0.86	0.88
C. Ex. 1	No	No	No	0.20	0.05
C. Ex. 2	Yes	No	No	0.48	0.12
C. Ex. 3	Yes	Yes	No	0.50	0.28
C. Ex. 4	Yes	Yes	No	0.52	0.32
C. Ex. 5	Yes	Yes	No	0.55	0.36

As is apparent from Tables 2 and 3, the polyimide FCCLs manufactured through the surface modification process of the present invention had adhesive strength of 0.8 kg/cm or more between the polyimide film and copper. In addition,

the polyimide FCCL, which had been subjected to an aging test under deterioration conditions of 150℃ for one week or more, was confirmed to maintain the adhesive strength of 0.7 kg/cm or more so as to assure sufficient adhesive strength even at high temperatures for a long period of time.

2. Measurement of Atomic Ratio on Polyimide

The surface of each of the polyimide CCLs manufactured in the examples and comparative examples was analyzed through ESCA to assay an atomic ratio.

The results of the atomic ratio analysis of the polyimide FCCL manufactured through the first plasma treatment, treatment with a coupling agent and second plasma treatment in Example 1 were compared to those of the CCL manufactured without surface modification in Comparative Example 1 and of the CCL manufactured through only the first plasma treatment in Comparative Example 2.

【Table 4】

Results of Measurement of Surface Atomic Ratio of Polyimide Film

No.	Surface Atoms of Polyimide			
	C1s	O1s	N1s	Si_2p
Comparative Example 1	72.714 %	19.422 %	7.864 %	-
Comparative Example 2	62.917 %	28.429 %	8.655 %	-
Example 1	54.490 %	30.848 %	7.795 %	6.686 %

From the result, it can be seen that the polyimide film modified in Example 1 has the silicon atom using the silane coupling agent, and has high oxygen content, thus realizing the polarized polyimide surface.

【Industrial Applicability】

As previously described herein, the present invention provides the polyimide film is subjected to a surface modification process including first plasma treatment, surface treatment through dipping in a solution containing a silane coupling agent and then second plasma treatment to modify the surface thereof. Thus, the above process is advantageous because it may substitute for a conventional surface treatment process using ion beams, and also does not use a specific seed layer, therefore decreasing the cost and reducing environmental contamination due to the use of heavy metals.

In addition, a polyimide FCCL having a two-layer structure is provided, and, in particular, a single-sided or double-sided polyimide FCCL can be provided by surface modifying either or both surfaces of the polyimide film.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

【CLAIMS】

【Claim 1】

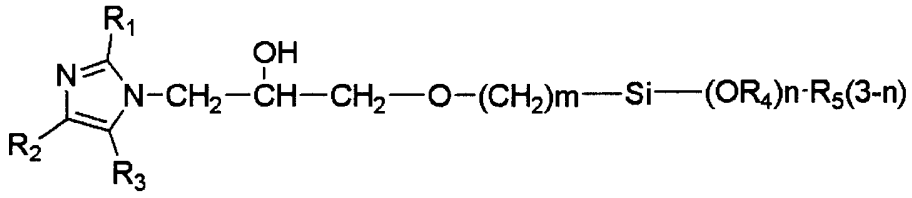
A method of surface modifying a polyimide film, comprising:

1) modifying surface of a polyimide film through first plasma treatment;

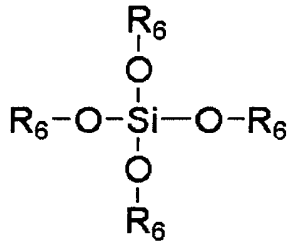
2) dipping the polyimide film into a solution containing a silane coupling agent, which is prepared by mixing a compound represented by Formula 1 below and a compound represented by Formula 2 below with mole ratio 1: 0.25~1 to treat the surface thereof; and

3) modifying surface of the polyimide film through second plasma treatment:

Formula 1



Formula 2



in Formulas 1 and 2, R_1, R_2 and R_3 are each hydrogen or a C_1~C_{10} alkyl group or vinyl group, R_4 and R_5 are each -(CH_2)x-, x is 1~4, R_6 is a C_1~C_5 alkyl group, aryl group or cyano group, m is 1~5 and n is 1~3.

【Claim 2】

The method according to claim 1, wherein the solution containing the silane coupling agent is prepared by using the silane coupling agent in an amount of 0.01~10 wt%.

【Claim 3】

The method according to claim 1, wherein the dipping process is conducted for 1~60 min.

【Claim 4】

The method according to claim 1, wherein the solution containing the silane coupling agent is prepared by dissolving a silane coupling agent in at least one or a

combination of solvents selected from the group consisting of water, acetone, methanol, ethanol, and isopropanol.

【Claim 5】

The method according to claim 1, wherein the treating a surface of the polyimide film with plasma is conducted at 20~100 W under pressure in a vacuum chamber of $1x10^{-3}$~$1x10^{-5}$ torr for 10~1,000 sec using a direct current or 60 Hz high-frequency power source.

【Claim 6】

A method of manufacturing a flexible copper clad laminate, comprising:

modifying a surface of a polyimide film using the method of surface modifying a polyimide film of claim 1;

copper sputtering either or both surfaces of the polyimide film at 0.5~30 mA and 50~500 W for 1~10 hours, to form a copper sputtering layer; and

electroplating the copper sputtering layer, to form a copper electroplating layer.

【Claim 7】

The method according to claim 6, wherein the copper sputtering layer has thickness of 500~5,000 Å.

【Claim 8】

The method according to claim 6, wherein the copper electroplating layer has thickness of 1~50 ㎛.

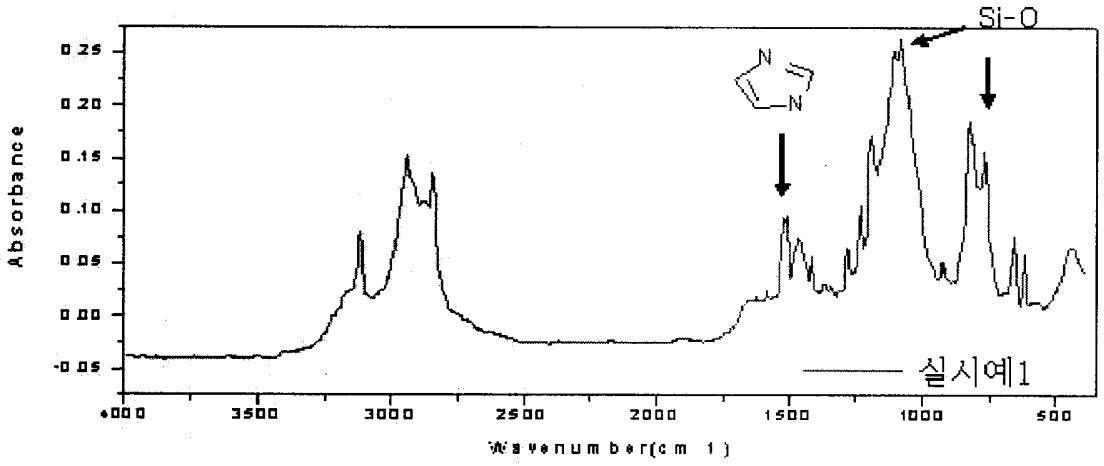
【Claim 9】

A polyimide flexible copper clad laminate having a two-layer structure, which comprises a 500~5,000 Å thick copper sputtering layer formed on either surface of the polyimide film which is modified using the method of claim 1; and a 1~50 ㎛ thick copper electroplating layer formed on the copper sputtering layer.

【Claim 10】

A polyimide flexible copper clad laminate having a two-layer structure, which comprises a 500~5,000 Å thick copper sputtering layer formed on each of both surfaces of the polyimide film which is modified using the method of claim 1; and a 1~50 ㎛ thick copper electroplating layer formed on the copper sputtering layer.

[Fig. 1]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Absorbance
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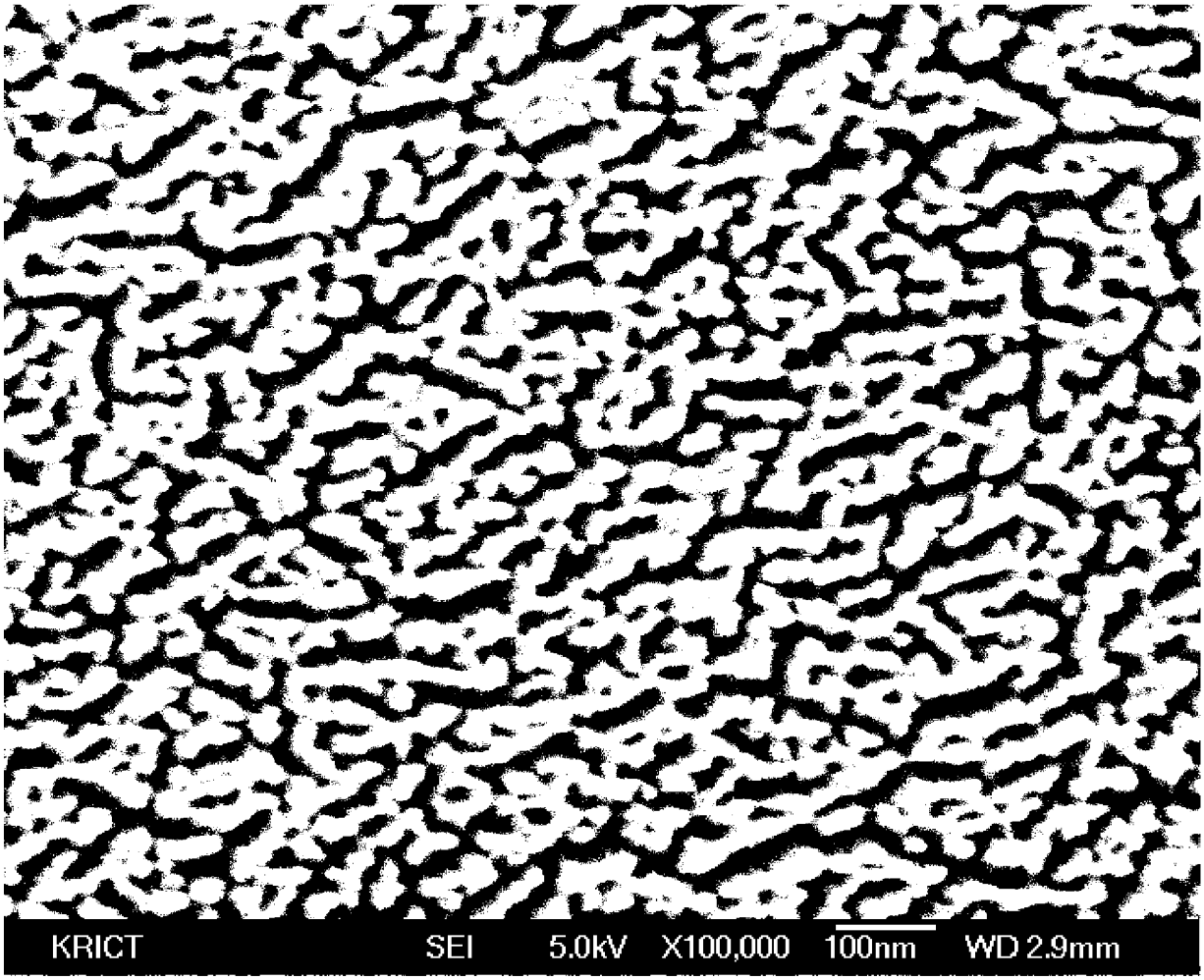
0.20
0.15
0.10
0.05
0.00
-0.05
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)
실시예1

[Fig. 2]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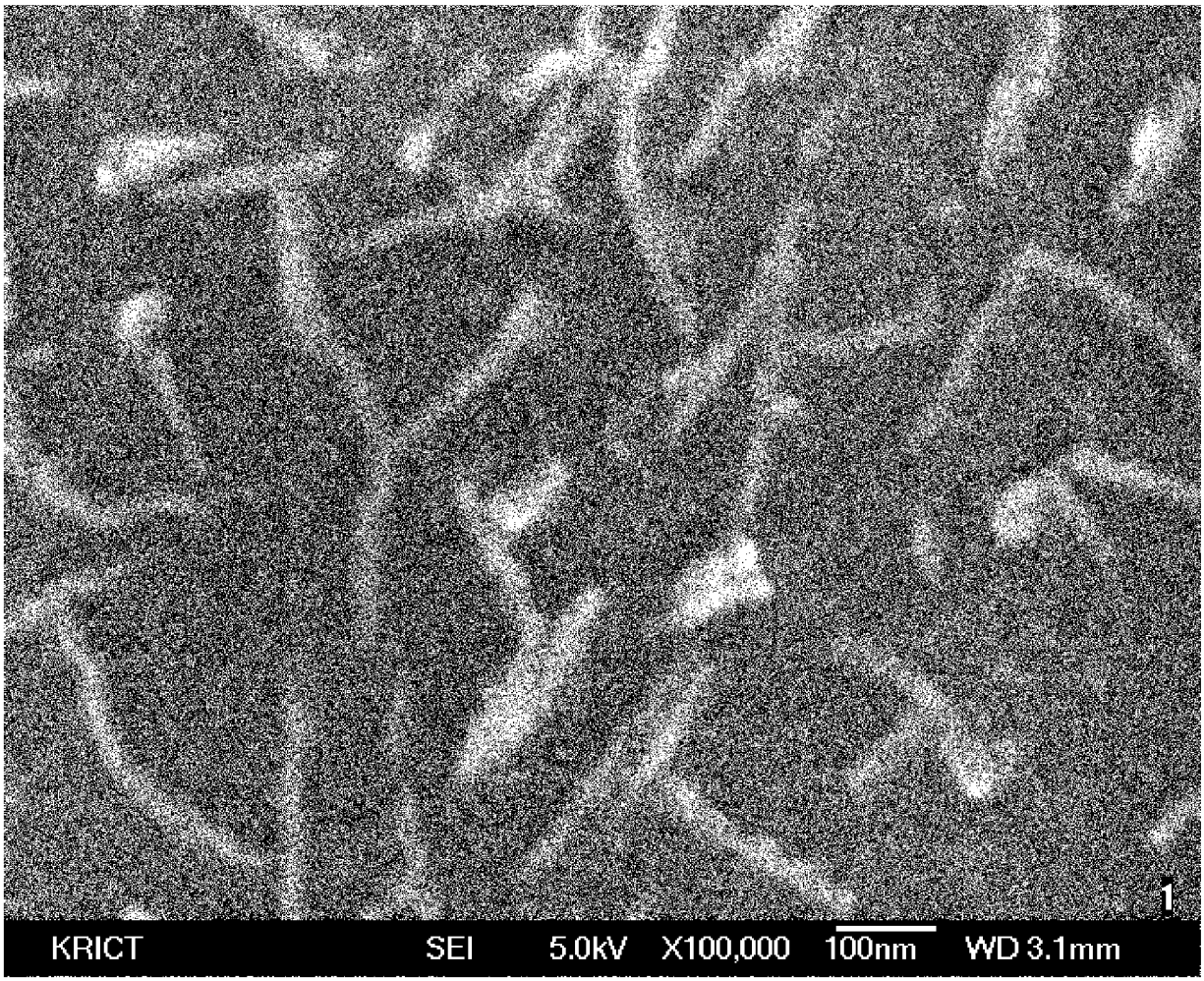
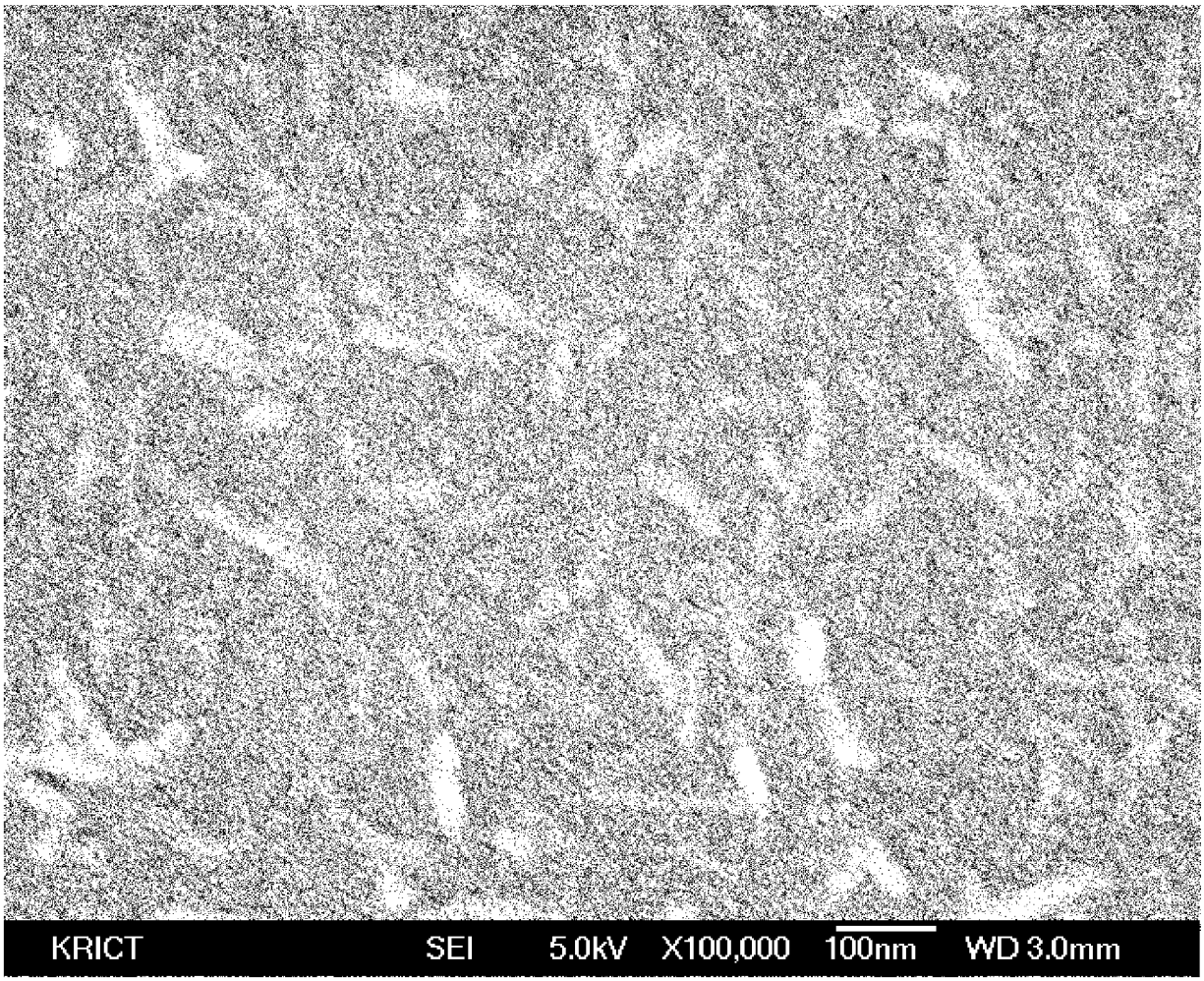
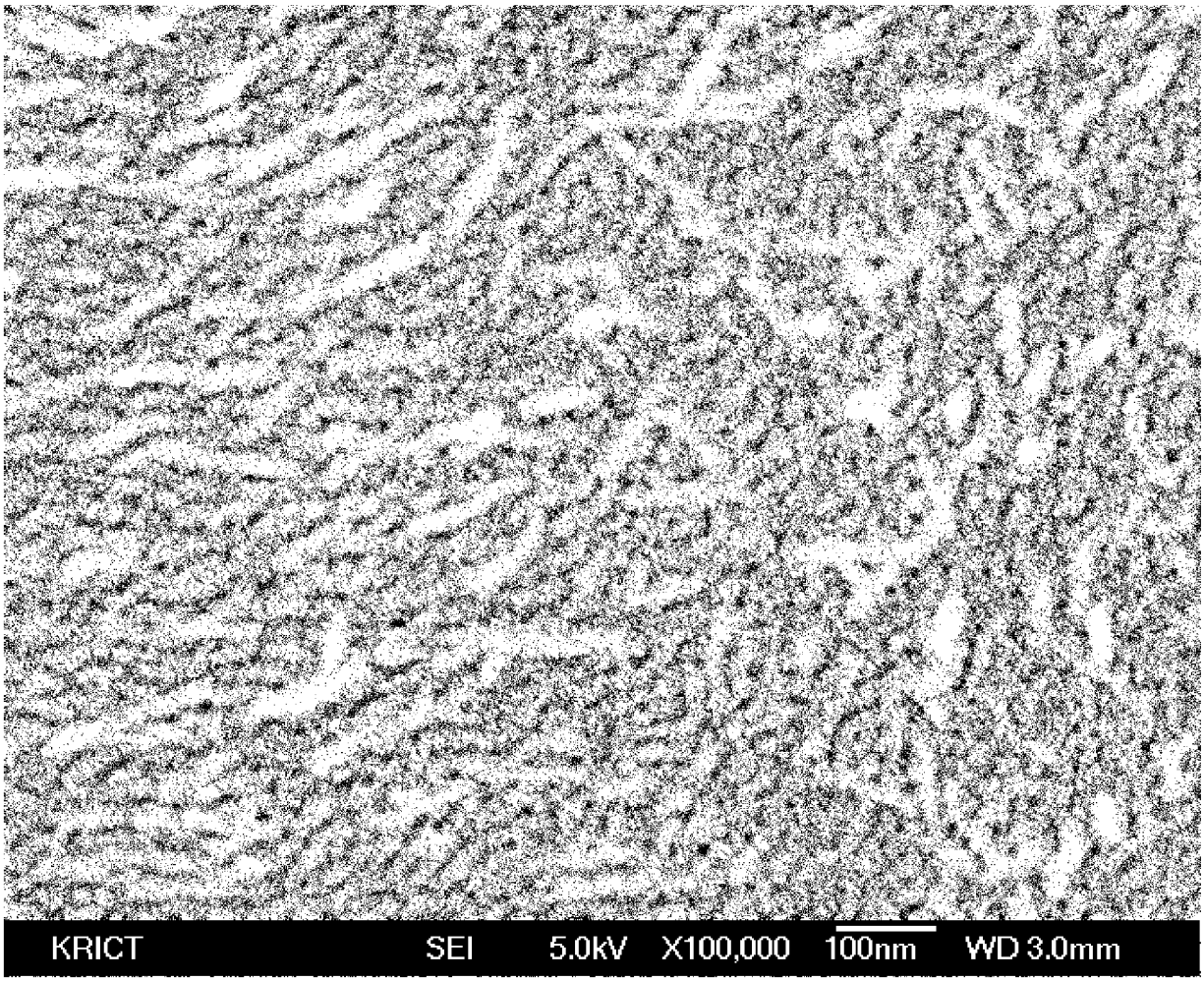
[Fig. 3]



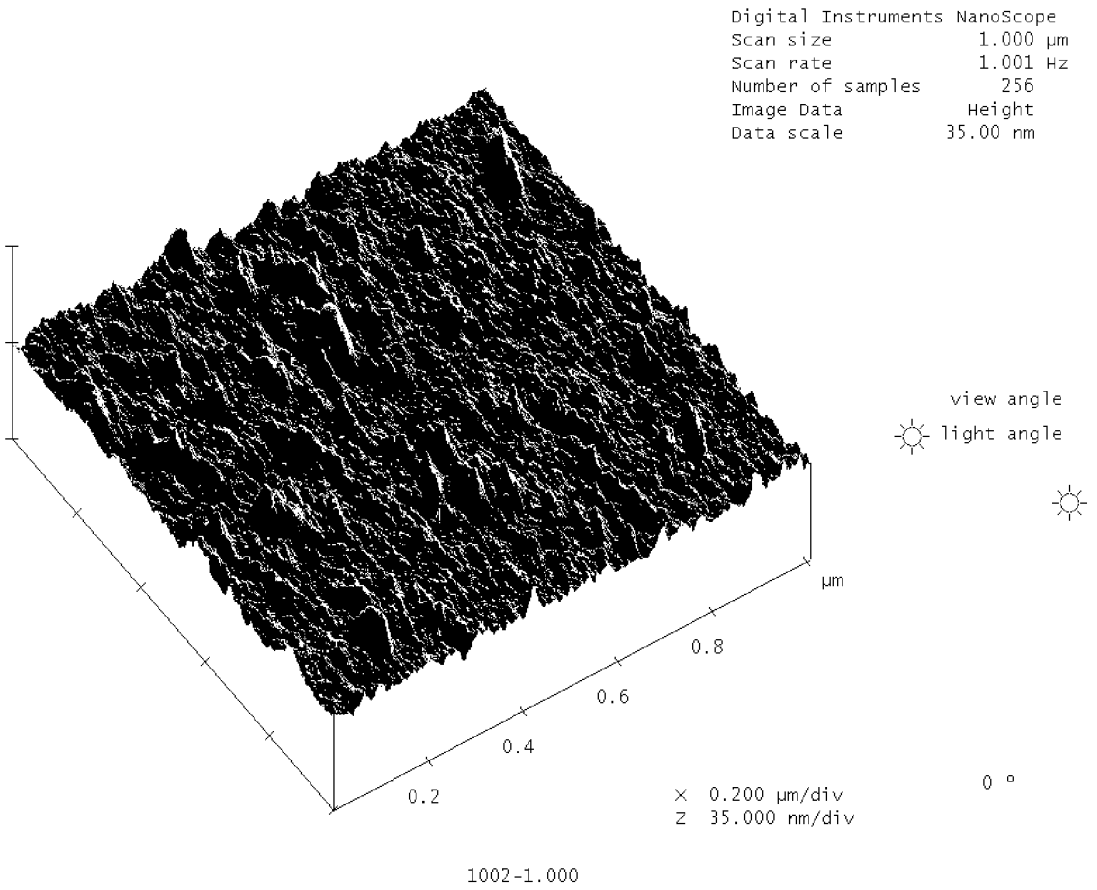
[Fig. 4]



[Fig. 5]



[Fig. 6]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X 0.200 µm/div
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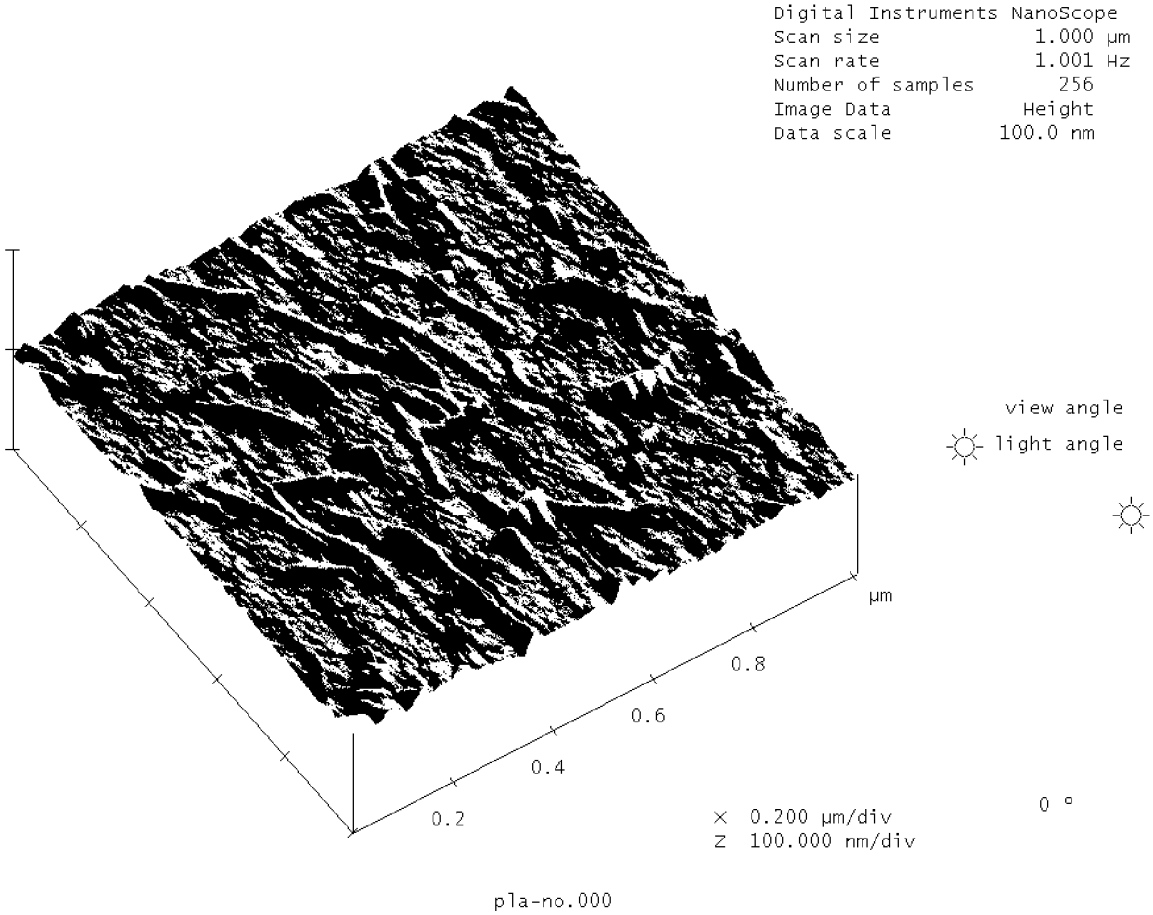
[Fig. 7]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light angle
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0 °
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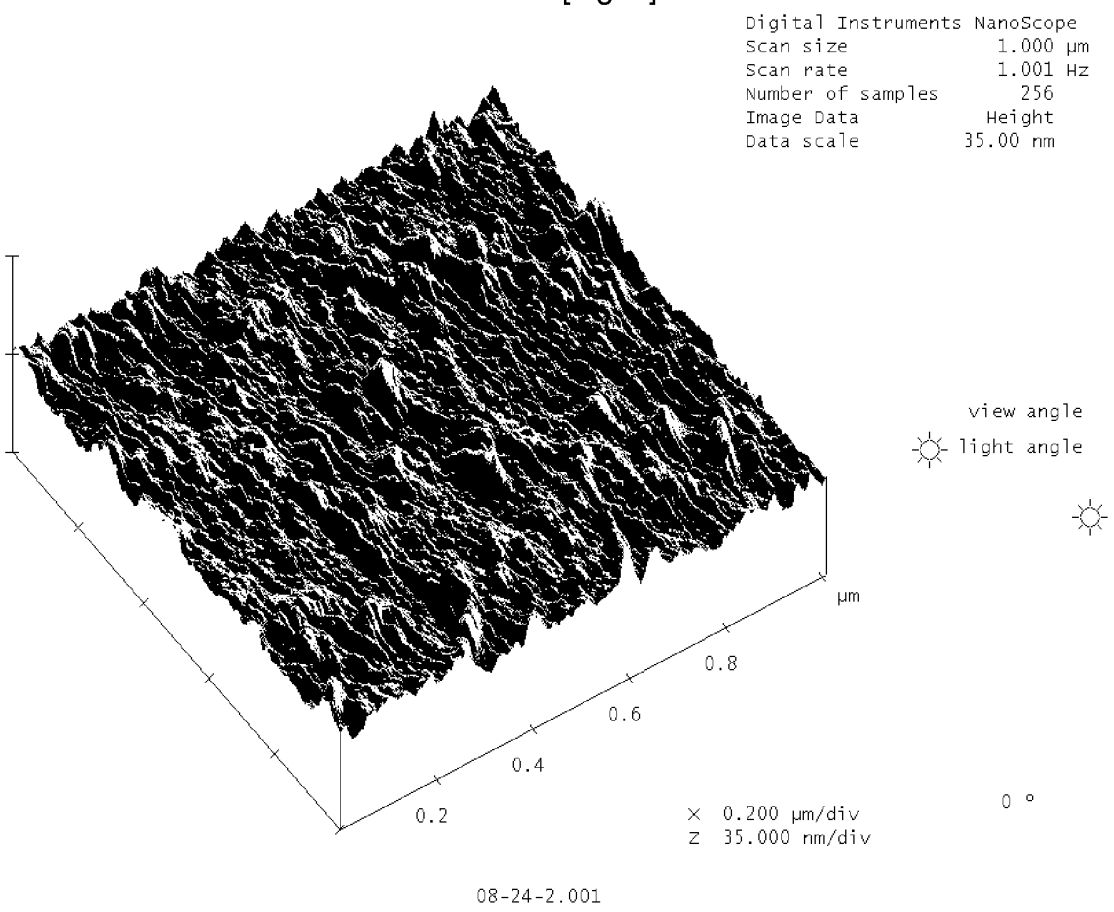
[Fig. 8]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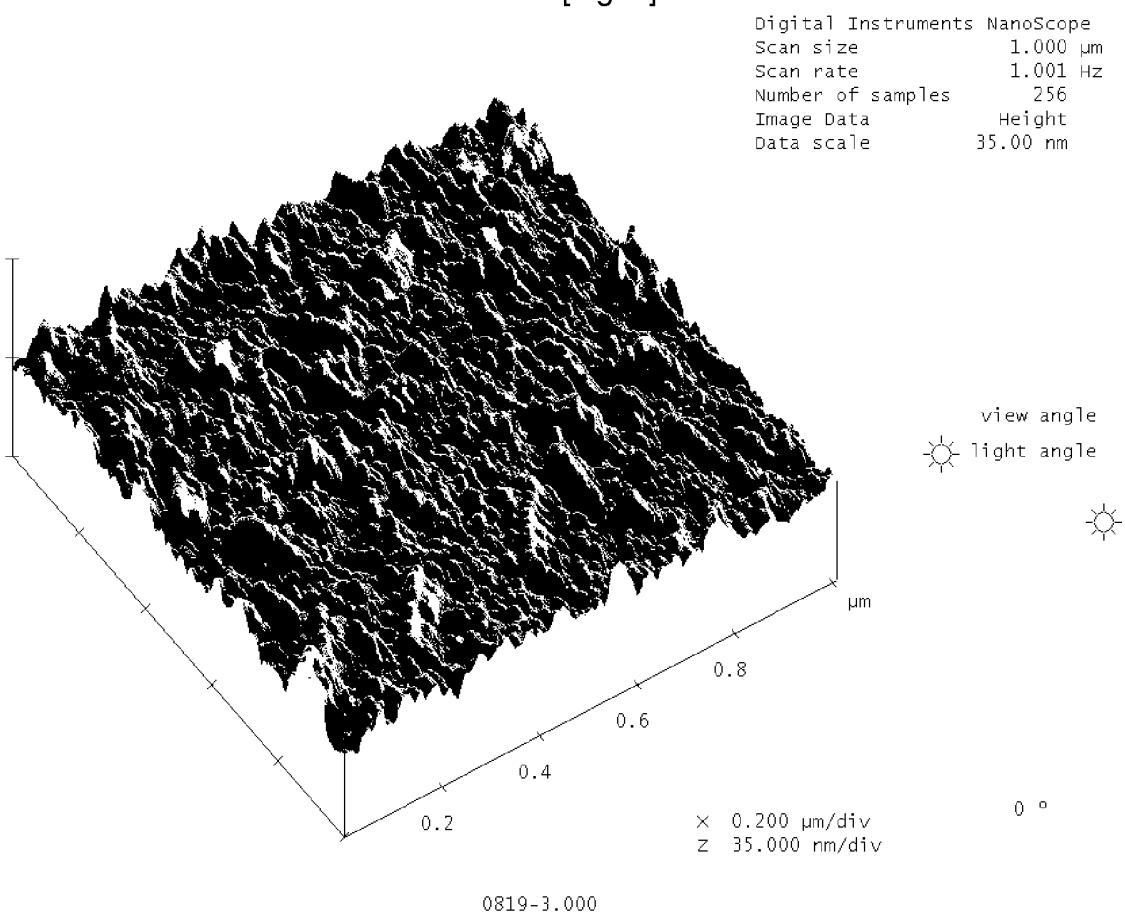
[Fig. 9]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µm
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0.4
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Z 35.000 nm/div
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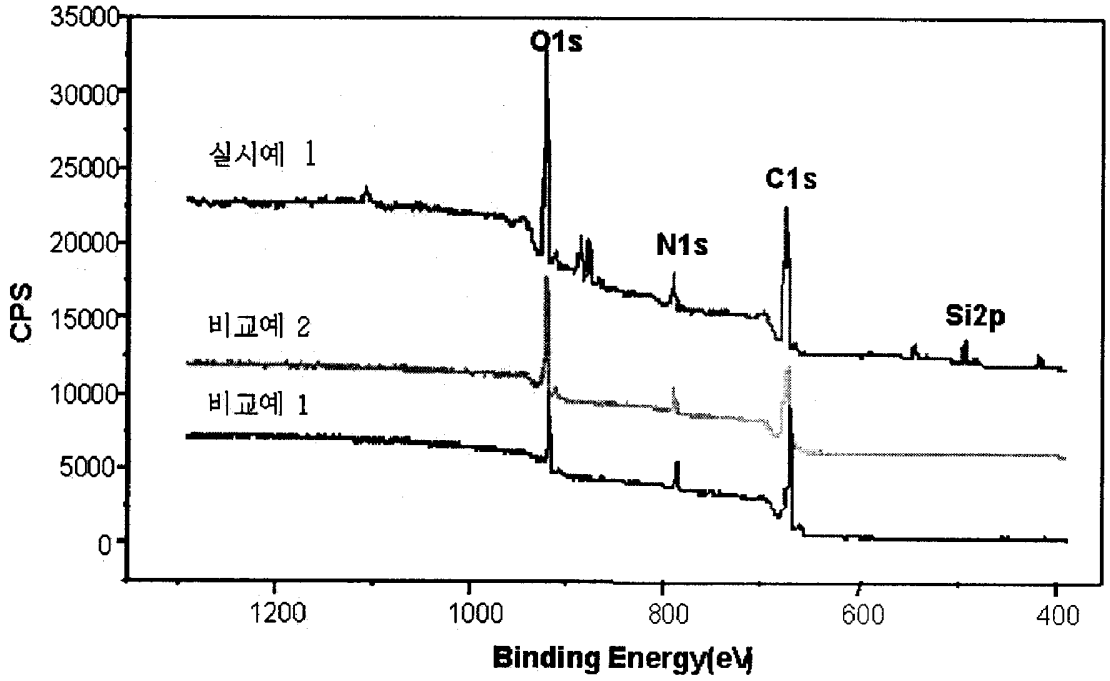
[Fig. 10]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CPS
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C1s
N1s
Si2p
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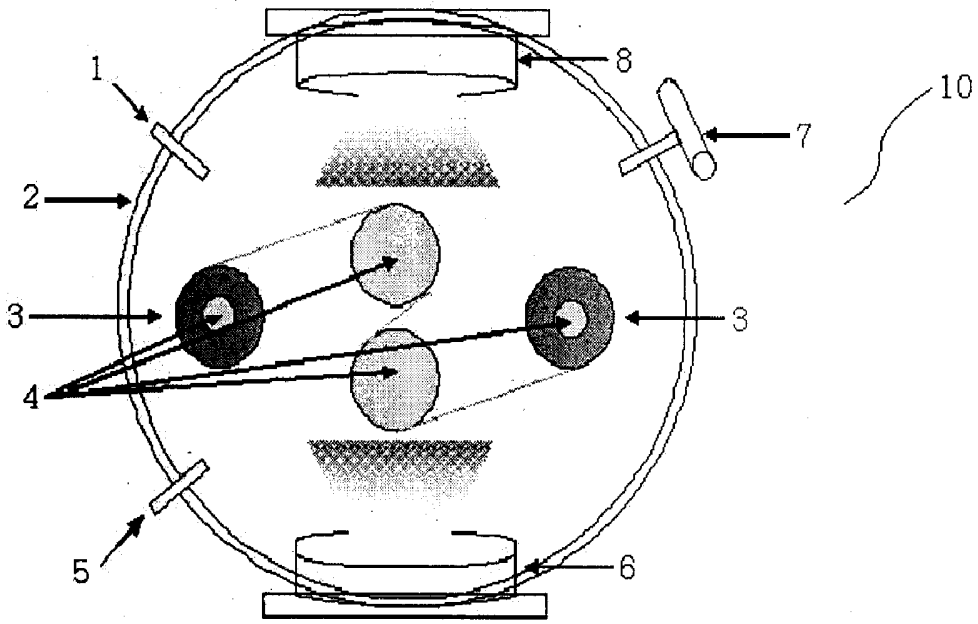
비교예 2
비교예 1
1200
1000
800
600
400
Binding Energy(eV)

[Fig. 11]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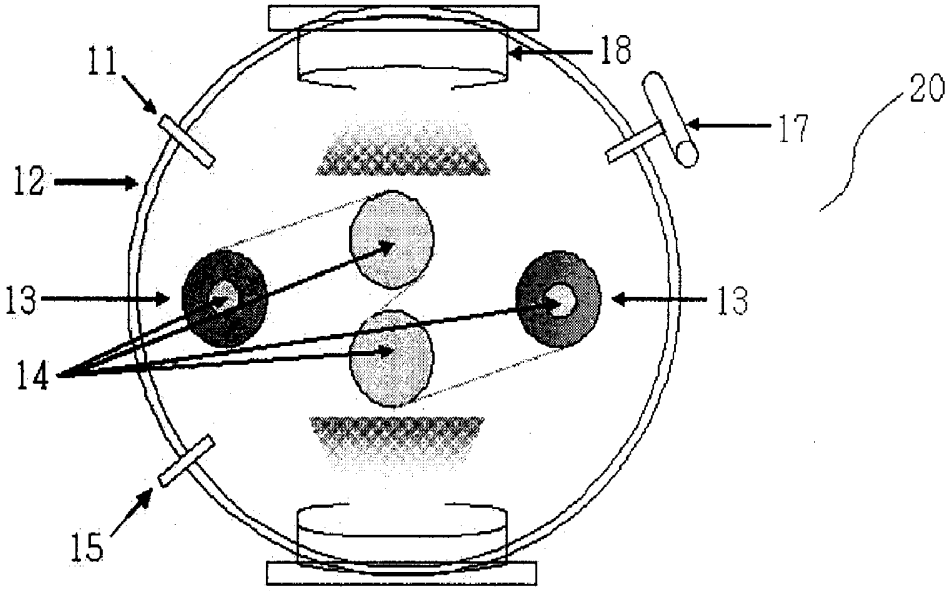
[Fig. 12]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/003816

A. CLASSIFICATION OF SUBJECT MATTER

C08J 7/12(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC8 C08J 7/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
KOREAN PATENTS AND APPLICATIONS FOR INVENTIONS SINCE 1975
KOREAN UTILITY MODELS AND APPLICATIONS FOR UTILITY MODELS SINCE 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
eKIPASS, SCOPUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Inagaki N. et al. "Improved adhesion between Kapton film and copper metal by silane-coupling reactions", Journal of Applied Polymer Science, 73(9), pp 1645-1654. 14 Jun. 1999 Whole document	1-10
A	JP 11-029852 A (TOMOEGAWA PAPER CO LTD) 2 Feb. 1999 Whole document	1-10
A	Ang, A.K.S. et al. "Low-temperature graft copolymerization of 1-vinyl imidazole on polyimide films with simultaneous lamination to copper foils- Effect of crosslinking agents", Polymer, 41(2), pp 489-498. 31 Jan. 2000 Abstract	1-10
A	Jang, J. et al. "Interfacial study of polyimide/copper system using silane-modified polyvinylimidazoles as adhesion promoters", Polymer, 42(7), pp 2871-2876. 31 Mar 2001 Abstract	1-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 FEBRUARY 2006 (20.02.2006)	**21 FEBRUARY 2006 (21.02.2006)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea	KANG, HYUNG SEOK
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5597

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/003816

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Kim, H. et al, "Corrosion protection and adhesion promotion for polyimide/copper system using silane-modified polymeric materials", Polymer, 41(17), pp 6553-6561. 31 Aug. 2000 Abstract	1
A	JP 2003-136632 A (ARAKAWA CHEM IND CO LTD) 14 May 2003 Claim 1	1
A	JP 2003-200527 A (ARAKAWA CHEM IND CO LTD) 15 Jul. 2003 Claim 1	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2005/003816

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JP15200527	15.07.2003	CN1578728A	09.02.2005
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		EP1447214A8	02.03.2005
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