



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 702 377 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.03.1996 Bulletin 1996/12

(51) Int Cl.⁶: **H01B 3/44**

(21) Application number: **95306237.9**

(22) Date of filing: **06.09.1995**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **06.09.1994 JP 212527/94**

(71) Applicant: **HITACHI, LTD.**
Chiyoda-ku, Tokyo 100 (JP)

(72) Inventors:
• **Nishimura, Shin**
Hitachi-shi, Ibaraki 316 (JP)

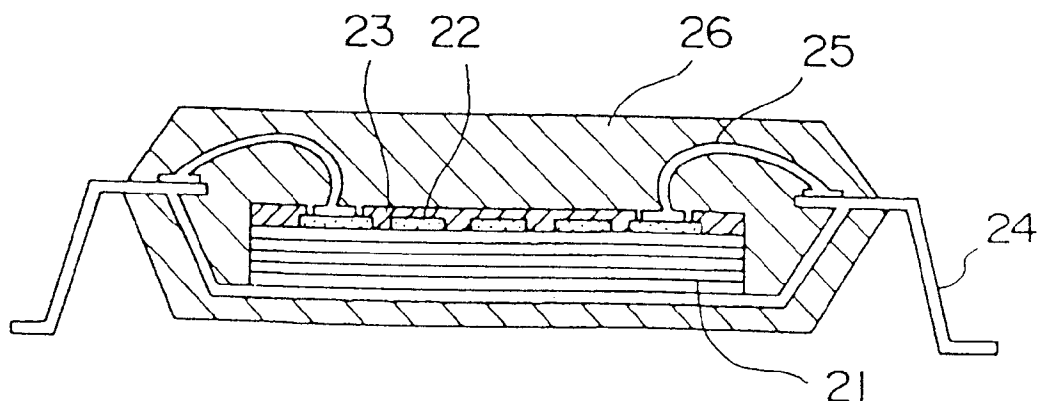
• **Saito, Toshiro**
Hitachi-shi, Ibaraki 316 (JP)
• **Takahashi, Akio**
Hitachiohta-shi, Ibaraki 313 (JP)

(74) Representative:
Calderbank, Thomas Roger et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) **Electronic device comprising organic thin film with high dielectric strength**

(57) Disclosed is an electronic device which comprises an electric substrate and an organic thin film with a high dielectric strength, wherein the organic thin film is formed on the surface of the substrate, and consists of a fluorine containing polymer having a molecular structure whose main chains are oriented substantially at the right angle with respect to the substrate and has an insulation strength of at least $1 \times 10^8 \text{V/m}$.

Fig. 3



EP 0 702 377 A2

Description

This invention is related to various electronic devices comprising an organic insulating film of high voltage strength.

As an insulating film of electronic devices, a film of polyimide or a vacuum deposition film of polyimide have heretofore been used. An example of forming a vacuum vapor deposition film of a polymer is reported wherein polypropylene is deposited in vacuum on alkaline halide substrate (J. Polym. Sci., Polym. Phys. ed., 16, 179 (1978)). And, as examples of fluorine containing polymers, there are reported vacuum deposition of vinylidene fluoridetrifluoroethylene copolymer (Rep. Prog. Polym. Phys. Jpn., 31, 183 (1988)), and vacuum deposition of polyvinylidene fluoride (preprints of Polymer Science Society, 43,). Generally speaking, a dielectric strength of polymers is influenced by water absorption properties, thermal resistance, agglomerated structure, crystallinity and dynamic properties.

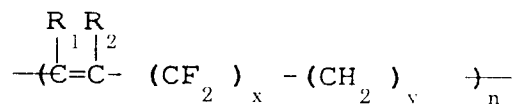
Dielectric strengths of various kinds of general-purpose polymers have been reported. For example, polytetrafluoroethylene is of $1.9\text{--}2.0 \times 10^7 \text{V/m}$, polypropylene is of $2.6 \times 10^7 \text{V/m}$, polystyrene is of $2.4 \times 10^7 \text{V/m}$, epoxy resin is of $1.9\text{--}2.0 \times 10^7 \text{V/m}$, and polyethylene is of $1.8 \times 10^7 \text{V/m}$. ("Electric Properties of High Polymers" by Kanamaru, Kyoritsu Publishing Co., Tokyo, 1981). However, when thin film of polymer is used as an insulation layer, a dielectric strength of the films is only about 10^7V/m because above-mentioned dielectric strengths becomes the upper limits for the thin films. Accordingly, a thickness of thin films need to be controlled to get a necessary dielectric strength, thus in the device in which a high voltage is applied, the film need to be made thick. For example, a thickness of approximately 10 microns is necessary to get a dielectric strength of 100V.

However, forming of such organic films by methods such as vacuum deposition, casting and spin coating is difficult. When a thickness of the film is large, the coloration is remarkable. Thus, the thick films are difficult to be used in such applications as solar batteries and displays where transmittance of light is important.

An object of the present invention is to provide an electronic device having an organic insulating thin film which has a high dielectric strength even if the thickness of the film is small.

Another object of this invention is to provide a semiconductor device which comprises an organic insulating thin film of high dielectric strength.

The general statement of this invention is as follows. In an electronic device of this invention, which has an organic insulating thin film of a high dielectric strength, the organic insulating thin film consists of a fluorine containing polymer having a molecular structure of which main chain (of the polymer molecule) are oriented substantially perpendicularly with respect to the surface of a substrate. And, the thin film has a dielectric strength of at least $1 \times 10^8 \text{V/m}$. The fluorine containing polymer is represented by the following general formula 1.



when R_1 and R_2 are CF_3 , $x=0$, $y=0$

or R_1 and R_2 are F, $x=2$, $y=0$

or R_1 is H and R_2 is F, $x=1$, $y=1$

Another object of this invention is achieved by a semiconductor device using the organic insulating thin film as insulating film. A vacuum deposition method and a plasma polymerization method which are dryprocesses are used as methods for forming homogeneous organic insulating thin films on a substrate. And, a spin coating method and a casting method using a solution or a casting method using a dispersed liquid are used as wetprocess. Because homogeneity and regularity of molecular orientation in the film can be superior, the vacuum deposition method is preferable as dry-process and spin coating method is preferable as wetprocess.

As polymers, following fluorine containing polymers are used; polytetrafluoroethylene, polyvinylidene fluoride, polytrifluoroethylene, poly(hexafluoro-1,3-butadiene), poly(hexafluoro-2-butyne), poly(1,1,2-trifluorobutadiene), poly(2,3,4,5,6-pentafluorostyrene) and their copolymers. In particular, preferable are fluorine containing polymers having regularity of agglomerated structure, high density, small water absorption properties, good thermal resistance, high crystallinity and high dynamic properties. And, in particular, poly(hexafluoro-1,3-butadiene) is preferable from the viewpoint of ease of vacuum deposition and solution preparation.

The polymer thin film of this invention is suited for application to the field such as various electronic devices, in particular solar batteries, displays, or EI elements in which transparency of insulation film is important. Because dielectric strength of the thin film of this invention is high, the thickness of the insulating film is approximately 1/10 of that of conventional thin film, thereby transparency of the thin film of the invention is superior to the conventional insulation films. Organic insulating thin films of this invention have a high, dense agglomerated structure of crystallinity wherein main chains are oriented substantially perpendicularly to the surface of the substrate. The insulating films of this invention exhibit high dynamic properties or high dielectric strength. And, moisture absorption that may cause insulation breakdown is suppressed by fluorine containing polymer. And, high dielectric strength is shown for high thermal resistance. As

fluorine containing polymer in case of polymers of hexafluoro-1,3-butadiene or hexafluoro-2-butyne or their copolymers. In addition to a characteristic as fluorine containing polymer when thin film is formed by vacuum deposition or casting and spin coating, crystallinity of thin film is high and the structure that main chain was oriented perpendicularly to the surface of the substrate or fine dielectric strength characteristic is shown.

In the drawings;

Fig. 1 is a block diagram of a vacuum deposition apparatus.

Fig. 2 shows FT-IR spectra of organic insulating thin films formed by vacuum deposition and of the polymer powder of raw material.

Fig. 3 shows the semiconductor package which comprises an organic insulating thin film of this invention.

Fig. 4 shows the module substrate which comprises organic insulating thin film of this invention.

In the following, this invention is explained by way of examples concretely, but it should be understood that the scope of this invention is not limited by following examples.

Example 1

A thin film was formed by a vacuum deposition method with poly(hexafluoro-1,3-butadiene).

Hexafluoro-1,3-butadiene is dissolved in toluene. After 2% cesium tert-butoxide (initiator) having been added to the monomer, the reaction product was re-precipitated in methanol after polymerization for 3 hours at 60 degrees centigrade and was refined to obtain poly(hexafluoro-1,3-butadiene). Vacuum deposition of thin film was carried out with a vacuum deposition apparatus made by Shimazu Seisakusho.

Fig. 1 is a diagram of the vacuum deposition apparatus. As shown in Fig. 1, in belljar 1 mounted on base plate 5, polymer specimen 3 put in tungsten basket 4 was set and substrate 2 is disposed on the specimen. In this example, pressure-molded pellets molded by means of a tablet molder at normal temperature were used as polymer specimen 3. As substrate 2, silicon plate, aluminum-deposited glass plate and glass plate with ITO film were used.

After the inside of belljar 1 was evacuated to be a vacuum degree of 2×10^{-5} Torr, by diffusion pump 6 and having done the polymer was deposited in vacuum on substrate 2 and test piece for measurement of voltage strength was prepared. Aluminum was furthermore deposited in vacuum as an electrode on the vacuum deposited polymer film of this test piece. A film thickness was measured by a slide needle type thickness meter. The film thickness was 0.5 microns. The molecular structure of vacuum deposition film prepared was examined by FT-IR (Furie transform infra-red absorption spectrometer). As shown in Fig. 2, reflection-absorption spectrum 12 of vacuum deposited polymer film on aluminum substrate and transmission spectrum 13 of vacuum deposited polymer film on silicon substrate were compared with spectrum 11 of KBr disk method of the raw material polymer. With respect to high sensitive refractive spectrum 12 of vacuum deposited polymer film, absorption 14 of vibration mode in a direction that was vertical on a plane of substrate 2 was observed. And, transmission spectrum 13 of vacuum deposited polymer film and absorption 15 of vibration mode in a direction that is parallel with the substrate 2 were observed. It was confirmed that main chains of the polymer were oriented substantially perpendicularly with respect to the surface of substrate 2 and the polymer had a high crystallinity. An insulating strength between aluminum electrodes deposited in vacuum on the test piece was measured.

The insulation breakdown voltage was measured by applying the voltage between the electrodes. Insulation breakdown happened at 125V. Accordingly, insulating strength was 2.5×10^8 V/m. The results are shown in Table 1.

Example 2

A thin film was formed by a vacuum deposition method with poly(hexafluoro-1,3-butadiene). Cesium fluoride of 2% (initiator) was added to hexafluoro-1,3-butadiene and was polymerized for 168 hours at 60 degrees in solvent THF (tetrahydrofuran). The reaction product was re-precipitated in methanol and refined to obtain poly(hexafluoro-1,3-butadiene). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 3

A thin film was formed by vacuum deposition method with poly(hexafluoro-1,3-butadiene). Cesium fluoride of 2% (initiator) was added to hexafluoro-1,3-butadiene and was polymerized for 168 hours at 60 degrees in toluene. The reaction reaction product was re-precipitated in methanol and refined to obtain poly(hexafluoro-1,3-butadiene). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 4

A thin film was formed by vacuum deposition method with poly(hexafluoro-2-butyne). Cesium fluoride of 2% (initiator) was added to hexafluoro-2-butyne and polymerized for 168 hours at 60 degrees in solvent THF. The reaction product was re-precipitated in methanol and was refined to obtain poly(hexafluoro-2-butyne). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 5

A thin film was formed by vacuum deposition method with poly(hexafluoro-1,3-butadiene-co-hexafluoro-2-butyne). Cesium tert-butoxide of 2% (initiator) was added to 1:1 mixed monomers of hexafluoro-1,3-butadiene and hexafluoro-2-butyne and was polymerized for 3 hours at 60 degrees in THF. The reaction product was re-precipitated in methanol and was refined to obtain poly(hexafluoro-1,3-butadiene-co-hexafluoro-2-butyne). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 6

A thin film was formed by a vacuum deposition method with poly(hexafluoro-1,3-butadiene). Cesium tert-butoxide of 2% (initiator) was added to hexafluoro-1,3-butadiene and was polymerized for 3 hours at 60 degrees in solvent THF. The reaction product was re-precipitated in methanol and was refined to obtain poly(hexafluoro-1,3-butadiene). The polymer was dissolved in hexafluorobenzene.

A polymer film was formed on substrate using the resulting solution by spin coating. As substrate, silicon plate, aluminum-deposited glass plate and glass plate with ITO film were used. In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 7

A thin film was formed by vacuum deposition method with poly(hexafluoro-1,3-butadiene). Cesium tert-butoxide of 2% (initiator) was added to hexafluoro-1,3-butadiene and was polymerized for 3 hours at 60 degrees in solvent THF. The reaction product was re-precipitated in methanol and was refined to obtain poly(hexafluoro-1,3-butadiene). The polymer was dissolved in hexafluorobenzene, and this polymer solution was coated on the substrate. The coated film was dried. As substrate, silicon plate, aluminum-deposited glass plate and glass plate with ITO film were used. In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Example 8

A thin film was formed by vacuum deposition method with poly(hexafluoro-1,3-butadiene). Cesium tert-butoxide of 2% (initiator) was added to hexafluoro-1,3-butadiene and was polymerized for 3 hours at 60 degrees in solvent THF. The reaction product was re-precipitated in methanol and was refined to obtain poly(hexafluoro-1,3-butadiene). The polymer was dispersed in water. This dispersion liquid was coated on the substrate and the coating was dried to form a film. As substrates, silicon plate, aluminum-deposited glass plate and glass plate with ITO film were used. In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Comparative Example 1

A thin film was formed by vacuum deposition method with polytetrafluoroethylene (Luburon L-5 made by Daikin Kogyo). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics of the film was carried out. The results are shown in Table 1.

Comparative Example 2

A thin film was formed by vacuum deposition method with poly(vinylidene fluoride) (Standard sample made by Sowa Kagaku). In the same manner as in Example 1, a polymer film was formed, and analysis and evaluation of characteristics

of the film was carried out. The results are shown in Table 1.

Table 1

	DIELECTRIC STRENGTH (10 ⁸ V/m OR MORE)	THE ORIENTATIONAL PROPERTY OF MEMBRANE
EXAMPLE 1	○	VERTICAL TO SUBSTRATE
EXAMPLE 2	○	VERTICAL TO SUBSTRATE
EXAMPLE 3	○	VERTICAL TO SUBSTRATE
EXAMPLE 4	○	VERTICAL TO SUBSTRATE
EXAMPLE 5	○	VERTICAL TO SUBSTRATE
EXAMPLE 6	○	VERTICAL TO SUBSTRATE
EXAMPLE 7	○	VERTICAL TO SUBSTRATE
EXAMPLE 8	○	VERTICAL TO SUBSTRATE
COMPARATIVE EXAMPLE 1	×	MANY PINHOLES
COMPARATIVE EXAMPLE 2	×	VERTICAL TO SUBSTRATE

In the table, ○ represents dielectric strength more than 10⁸V/m, and × represents less than 10⁸V/m.

As shown in Table 1, organic insulating thin films of this invention had high degree of crystallization and high orientation of main chains so that they exhibited high dielectric strength, compared with polymer films comparative examples.

Various kinds of devices were prepared with insulation films whose characteristics were identified in the examples.

Example 9

A solar battery which comprises an organic insulating thin film of this invention was prepared by a vacuum deposition method with poly(hexafluoro-1,3-butadiene) shown in Example 1 as an insulating material. The polymer insulating film, a silicon series solar battery element and another polymer insulating film were successively formed on a silicon substrate to constitute a solar battery.

Example 10

An EL element (electro-luminescence element) which comprises poly(hexafluoro-1,3-butadiene) as a polymer insulating film of this invention was prepared by a vacuum deposition method.

The polymer insulation film, an aluminum thin film electrode, EL element, another aluminum thin film electrode and another polymer insulation film were successively formed on a silicon substrate to constitute the EL element.

Example 11

A semiconductor element which comprises a coating of poly(hexafluoro-1,3-butadiene) shown in Example 1 as a passivation film that was formed by a vacuum deposition method was prepared. The semiconductor element was a molded with packaging material to obtain a semiconductor package. This package is constituted as follows.

As shown in Fig. 3, aluminum wiring 22 was deposited in vacuum on silicon chip 21. Then, polymer insulation film 23 was deposited in vacuum to cover wiring 22. Aluminium wire 22 and terminals of lead frame 24 on the circumference of chip 21 were connected by gold wires 25. Finally, the element was molded by packaging material 26.

Example 12

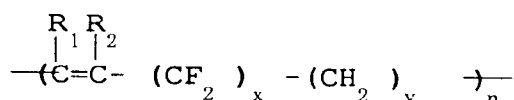
A module substrate which comprises poly(hexafluoro-1,3-butadiene) shown in Example 1 as a polymer insulation film of this invention that was formed by a vacuum deposition method was prepared. As shown in Fig. 4, copper wiring 29a was formed on ceramic substrate 28 of multilayer wiring, and polymer insulation film 30 was deposited in vacuum to cover wiring 29a. Then, copper wiring 29b was formed on insulation film 30 to constitute the module substrate. According to this invention, compared with conventional organic insulating thin films, dielectric strength of the thin films of the invention is excellent. The necessary dielectric strength for insulating films can be realized with a thickness of 1/10 that of conventional films. Improvement of efficiency in devices such as display, solar batteries, EL element in which transparency is particularly needed can be expected.

Claims

1. An electronic device which comprises an electronic substrate and an organic thin film with a high dielectric strength, wherein the organic thin film is formed on the surface of the substrate, and consists of a fluorine containing polymer having a molecular structure whose main chains are oriented substantially at the right angle with respect to the surface of the substrate and has an insulation strength at least $1 \times 10^8 \text{V/m}$.

2. An electronic device which comprises an electronic substrate and an organic thin film with a high dielectric strength, wherein the organic thin film is formed on the surface of the substrate, and consists of a crystalline fluorine containing polymer and has an insulation strength of at least $1 \times 10^8 \text{V/m}$.

3. An electronic device which comprises an electronic substrate and an organic thin film with a high dielectric strength, wherein the organic thin film is formed on the surface of the substrate, and the polymer is represented by the following general formula, and has an insulation strength of at least $1 \times 10^8 \text{V/m}$.



when R_1 and R_2 are CF_3 , $x=0$, $y=0$
 or R_1 and R_2 are F, $x=2$, $y=0$
 or R_1 is H and R_2 is F, $x=1$, $y=1$

4. The electronic device according to claim 1, wherein the thin film is formed by a vacuum deposition method with a fluorine containing polymer.

5. The electronic device according to claim 1, wherein the thin film is formed by a casting method with a solution of the fluorine containing polymer.

6. The electronic device according to claim 1, wherein the thin film is formed by a casting method with a dispersion solution of the fluorine containing polymer.

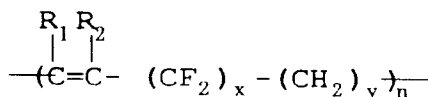
7. The electronic device according to claim 1, wherein the thin film is formed by a spin-coating method with a solution of the fluorine containing polymer.

8. A semiconductor device which comprises a semiconductor element having at least one pn-junction exposed to the surface thereof and an organic thin film with a high dielectric strength, wherein the organic thin film is formed on at least the surface of the exposed pn-junction, and consists of a crystalline fluorine containing polymer having a molecular structure whose main chains are oriented substantially at the right angle with respect to the surface of the substrate.

9. The semiconductor device according to claim 8, wherein the thin film is formed by a spin-coating method with a solution of the fluorine containing polymer.

10. The semiconductor device according to claim 8, wherein the thin film has an insulation strength at least $1 \times 10^8 \text{V/m}$.

11. The semiconductor device according to claim 8, wherein the polymer of the thin film is represented by the following general formula.



when R_1 and R_2 are CF_3 , $x=0$, $y=0$
 or R_1 and R_2 are F, $x=2$, $y=0$
 or R_1 is H and R_2 is F, $x=1$, $y=1$

Fig. 1

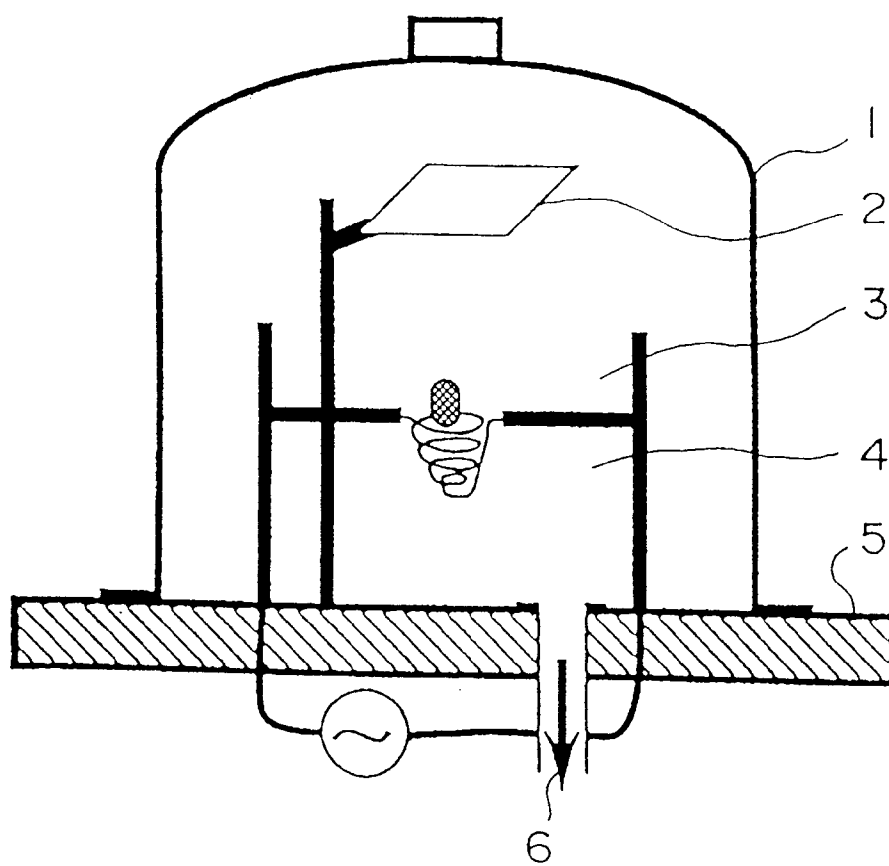


Fig. 2

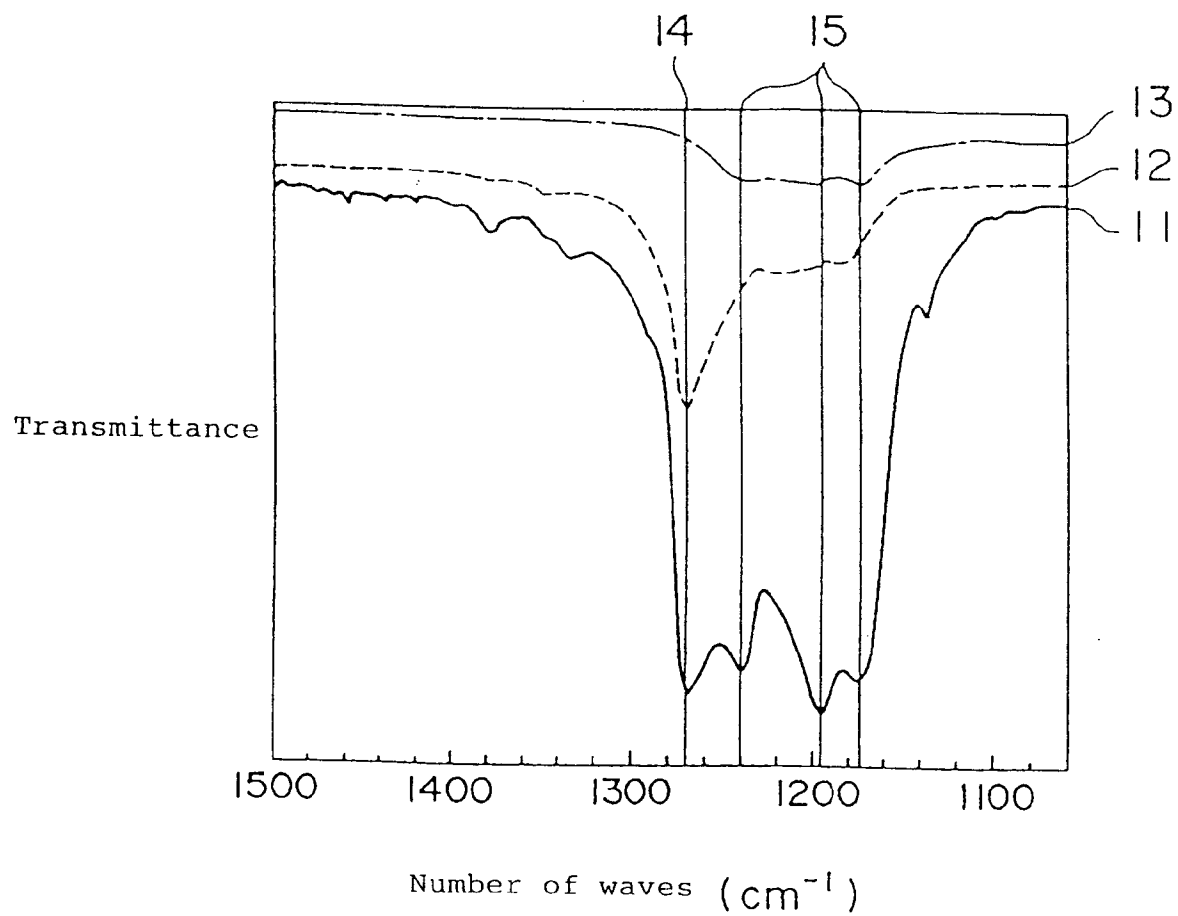


Fig. 3

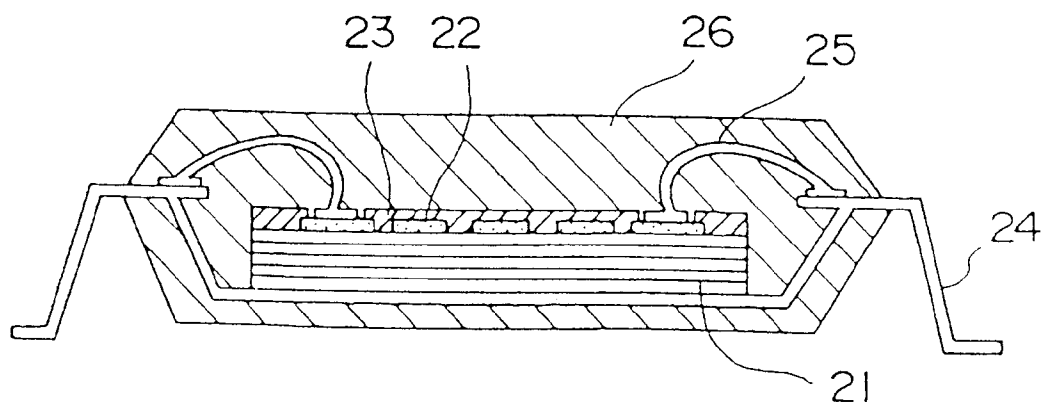


Fig. 4

