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Integrated circuit comprising an organic semiconductor,
and method for the production of an integrated circuit

- 5 The invention relates to an integrated circuit according to the preamble of claim 1 and to a process for producing an integrated circuit comprising an organic semiconductor as claimed in claim 9.
- 10 Systems comprising integrated circuits based on organic semiconductors, in particular organic field effect transistors (OFET), constitute a promising technology in the mass application sector of economical electronics. A field effect transistor is considered to
- 15 be organic particularly if the semiconducting layer is produced from an organic material.

Since it is possible to build up complex circuits using OFETs, there are numerous potential applications. Thus,

20 for example, the introduction of RF-ID (RF-ID: radio frequency identification) systems based on this technology is considered as a potential replacement for the bar code, which is susceptible to faults and can be used only in direct visual contact with the scanner.

25 In particular, circuits on flexible substrates, which can be produced in large quantities in roll-to-roll processes, are of interest here.

- 30 Owing to the thermal distortion of most suitable economical substrates (e.g. polyethylene terephthalate (PET), polyethylene naphthalate (PEN)), there is an upper temperature limit of 130 - 150°C for the production of such flexible substrates. Under certain
- 35 preconditions, for example a thermal pretreatment of the substrate, this temperature limit can be increased to 200°C



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but with the restriction that, although the distortion of the substrate is reduced, it is not prevented.

5 A critical process step in the case of electronic components is the deposition of the dielectric layer, in particular the gate dielectric layer, of an OFET. The quality of the dielectrics in OFETs has to meet very high requirements with regard to the thermal, chemical, mechanical and electrical properties.

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Silicon dioxide (SiO_2) is the currently most frequently used gate dielectric in OFETs, based on the wide availability in semiconductor technology. Thus, transistor structures in which a doped silicon wafer serves as the gate electrode, and thermal SiO_2 grown thereon forms the gate dielectric are described. This SiO_2 is produced at temperatures of about 800 - 1000°C. Other processes (e.g. CVD) for the deposition of SiO_2 on various substrates likewise operate at temperatures above 400°C. A group at PennState University has developed a process (ion beam sputtering) which makes it possible to deposit a high-quality SiO_2 at process temperatures of 80°C. This is described in the articles by C.D. Sheraw, J.A. Nichols, D.J. Gunlach, J.R. Huang, 15 C.C. Kuo, H. Klauk, T.N. Jackson, M.G. Kane, J. Campi, F.P. Cuomo and B.K. Greening, Techn. Dig. -lot. Electron Devices Meet., 619 (2000), and C.D. Sheraw, L. Zhou, J.R. Huang, D.J. Gundlach, T.N. Jackson, M.G. Kane, I.G. Hili, M.S. Hammond, J. Campi, 25 B.K. Greening, J. Francl and J. West, Appl. Phys. Lett. 80, 1088 (2002). 30

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However, the high process costs and the low throughput are disadvantageous here for mass-produced products.

It is also known that inorganic nitrides, such as, for example, SiN_x , TaN_x , can be used. Similarly to the preparation of inorganic

oxides, the deposits of inorganic nitrides require high temperatures or high process costs. This is described, for example, in the article by B.K. Crone, A. Dodabalapur, R. Sarpeshkar, R.W. Filas, Y.Y. Lin, 5 Z. Bao, J.H. O'Neill, W. Li and H.E. Katz, J. Appl. Phys. 89, 5125 (2001).

It is also known that hybrid solutions (spin on glass) can be used. Organic siloxanes which can be prepared 10 from a solution and can be converted into "glass-like" layers by thermal conversion were described. The conversion into SiO_2 is effected either at high temperatures (about 400°C) or takes place only partly, which results in a reduced transistor quality (in this 15 context, cf. the article by Z. Bao, V. Kuck, J.A. Rogers and M.A. Paczkowski, Adv. Funct. Mater., 12, 526 (2002)).

In addition, organic polymers, such as, for example, 20 poly-4-vinylphenol (PVP), poly-4-vinylphenol-co-2-hydroxyethyl methacrylate or polyimide (PI), have already been used. These polymers are distinguished by their comparatively simple processibility. Thus, they can be used, for example, from solution for spin 25 coating or printing. The outstanding dielectric properties of such materials have already been demonstrated (cf. article by H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik and W. Weber, J. Appl. Phys., in press, scheduled to appear in vol. 92, 30 no. 10 (November 2002)).

It has also already been possible to demonstrate applications in interconnect layers (ICs), the required chemical and mechanical stabilities of the dielectric 35 layers for the structuring thereof and the structuring of the subsequent source-drain layer having been achieved by crosslinking of the polymers (cf. article by M. Halik, H. Klauk, U. Zschieschang, T. Kriem, G. Schmid and W. Radlik, Appl. Phys. Lett., 81, 289 (2002)).

However, this crosslinking is effected at temperatures of 200°C, which is problematic for the production of flexible substrates having a large area.

5 It is the object of the present invention to provide an integrated circuit comprising an organic semiconductor and a method in which the production of dielectric layers of OEFTs is possible at low temperatures.

10 This object is achieved, according to the invention, by a method having the features of claim 1.

According to the invention, the integrated circuit comprising an organic semiconductor can be produced
15 from a polymer formulation consisting of

- a) 100 parts of at least one crosslinkable base polymer,
- b) from 10 to 20 parts of at least one di- or
20 tribenzyl alcohol compound as the electrophilic crosslinking component,
- c) from 0.2 to 10 parts of at least one photo acid generator and
- d) at least one solvent.

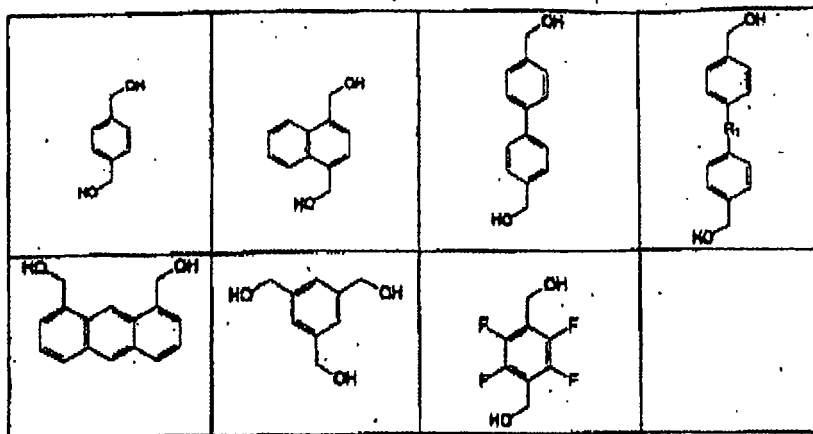
25 The integrated circuits according to the invention are in particular OFETs having organic layers, which have outstanding dielectric properties. Owing to the specific polymer formulation used, the integrated
30 circuits can be produced in a simple manner at low temperatures (up to 150°C). This polymer formulation can also be used in principle in combination with other electronic components.

35 It is advantageous if at least one base polymer is a phenol-containing polymer or copolymer, in particular poly-

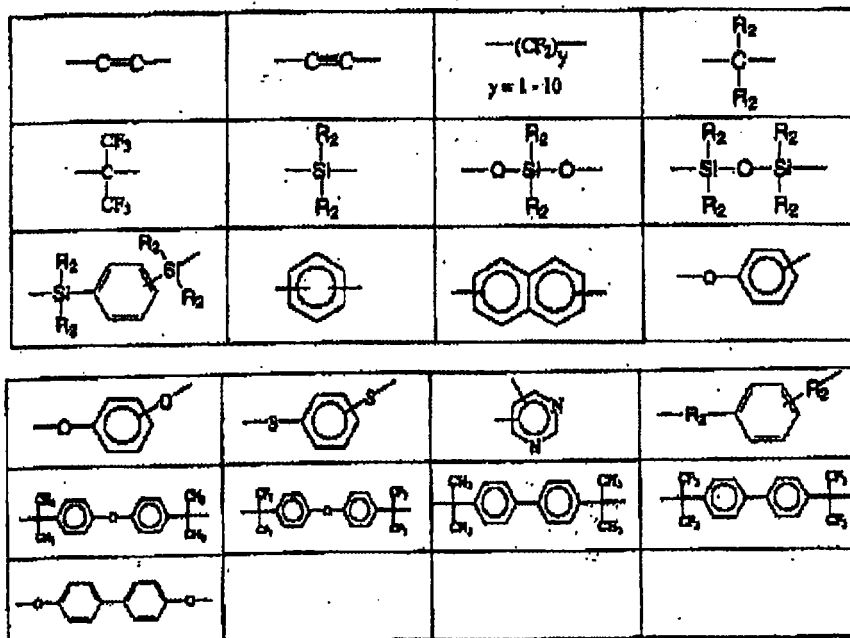
4-vinylphenol, poly-4-vinylphenol-co-2-hydroxyethyl
methacrylate or poly-4-vinylphenol-co-methyl
methacrylate.

- 5 Advantageously, at least one di- or tribenzyl alcohol
compound as electrophilic crosslinking component is 4-
hydroxymethylbenzyl alcohol.

10 It is advantageous if at least one crosslinking
component has one of the following structures:



The following is true for R_1 : $-O-$, $-S-$, $-SO_2-$, $-S_x-$, $-(CH_2)_x-$, in which $x = 1 - 10$, and additionally:



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The following is true for R_2 : alkyl having 1 to 10 carbon atoms or aryl

Advantageously, the photo acid generator used is at least one compound which, on exposure to UV light, generates a photo acid for transferring a proton to the hydroxyl group of a benzyl alcohol, in particular a sulfonium or an iodonium salt.

Advantageous solvents are an alcohol, in particular n-butanol, propylene glycol monomethyl ethyl acetate (PGMEA), dioxane, N-methylpyrrolidone (NMP), γ -butyrolactone, xylene or a mixture.

For good processibility, it is advantageous if the proportion of base polymer, crosslinking component and photo acid generator is a proportion between 5 and 20% by mass.

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The object is also achieved by a method for the production of an integrated circuit, in particular of an OFET, comprising a dielectric layer, having the features of claim 1. According to the invention

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a) a polymer formulation as claimed in claim 1 is applied to a substrate, in particular having a prestructured gate electrode, and then

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b) a photoinduced crosslinking reaction for the formation of the gate dielectric layer is carried out.

For the production of an OFET, at least one further structuring for producing the OFET is then advantageously carried out.

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The photoinduced crosslinking reaction is advantageously initiated by exposure to UV radiation. It is particularly advantageous if, after the exposure, a heating step, in particular a post exposure bake, is effected. It is advantageous if the temperature in the heating step is not more than 140°C, in particular 100°C. After the post exposure bake (PEB), it is advantageous if at least one further structuring for producing the OFET is effected.

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The application of the polymer formulation is preferably effected by spin coating, printing or spraying.

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The crosslinking reaction is advantageously effected under an inert gas atmosphere, in particular an N₂ atmosphere.

After the application of the polymer formulation and the production of the polymer film, it is advantageous to carry out drying, in particular at 100°C.

- 5 For the production of the OFET, it is then advantageous to apply a source-drain layer to the gate dielectric layer.

10 Finally, it is advantageous if an active layer for the formation of an OFET, in particular comprising the semiconducting pentacene, is applied to the source-drain layer. A passivating layer is advantageously arranged on the active layer.

- 15 The invention is explained in more detail below for a plurality of embodiments with reference to the figures of the drawings.

20 Fig. 1 shows a schematic diagram of an organic field effect transistor;

25 Fig. 2 shows an example of a photoinduced crosslinking reaction of a polymeric gate dielectric comprising PVP and 4-hydroxymethylbenzyl alcohol as a crosslinking agent;

30 Fig. 3a shows a family of output characteristics of an OFET comprising an electrophilically crosslinked gate dielectric;

35 Fig. 3b shows a family of transmission characteristics of an OFET comprising an electrophilically crosslinked gate dielectric;

Fig. 4 shows a trace of an oscilloscope image

OFETs are electronic components which consist of a plurality of layers, all of which have been structured, in order to generate integrated circuits by connections
5 of individual layers.

Fig. 1 shows the fundamental structure of such a transistor in a bottom contact architecture.

5 A gate electrode 2, which is covered by a gate dielectric layer 3, is arranged on a substrate 1. As will be explained later, in an embodiment of the process according to the invention the substrate 1 with the gate electrode 2 already arranged thereon constitutes the starting material on which the gate
10 dielectric layer 3 is applied. A drain layer 4a and a source layer 4b, both of which are connected to the active semiconducting layer 5, are arranged on the gate dielectric layer 3. A passivating layer 6 is arranged above the active layer 5.

15 The source layer 4b produces a connection to the interconnect layer 7.

20 The deposition and processing of the gate dielectric layer 3 are decisive for that embodiment of the invention which is described here.

25 The circuits according to the invention and the production thereof solve the problem of the provision of OFETs having gate dielectric layers, in particular with organic ICs having outstanding mechanical, chemical and electrical properties in combination with low process temperatures.

30 An OFET has a dielectric layer which can be produced from a mixture (polymer formulation) comprising in principle four components: a base polymer, a crosslinking component, a photo acid generator and a solvent. An embodiment of the circuit according to the
35 invention which is mentioned here by way of example has a polymer formulation comprising the following components

a) PVP as the crosslinkable base polymer,

b) 4-hydroxymethylbenzyl alcohol as an electrophilic crosslinking component,

c) triphenylsulfonium hexaflate as the photo acid generator (PAG),

d) e.g. alcohols, PGMEA as the solvent.

This polymer formulation is applied to a correspondingly prepared substrate 1 (gate structures 2 have already been defined on the substrate 1). The polymer formulation can be applied, for example, by printing, spin coating or spray coating. By subsequent drying at moderate temperatures (about 100°C), the polymer formulation is fixed on the substrate.

Thereafter, an exposure step using UV light is effected, the wavelength and the duration of the UV irradiation being dependent on the photo acid generator used. A photo acid, which initiates a crosslinking reaction in a subsequent heating step (not more than 140°C, post exposure bake (PEB)), is generated from the photo acid generator.

Fig. 2 shows the photoinduced electrophilic crosslinking reaction of a polymeric gate dielectric for PVP by way of example with 4-hydroxymethylbenzyl alcohol as the crosslinking component. The photo acid generator used is triphenylsulfonium hexaflate.

As a result of the photochemically induced crosslinking reaction, solubility differences are produced between crosslinked and uncrosslinked material. By using masks, a definition of exposed and unexposed parts is possible thereby, which can be used for structuring the gate dielectric layer 3.

The use of the process reduces the required crosslinking temperature by more than 60°C compared with the

methods known to date (cf. article by Halik et al. (2002)). The temperatures used are not critical for the substrate.

- 5 The base polymer determines the fundamental properties of the gate dielectric layer 3. Suitable base polymers are in principle all phenol-containing polymers and copolymers thereof, such as, for example, poly-4-vinylphenol, poly-4-vinylphenol-co-2-hydroxyethyl
10 methacrylate or poly-4-vinylphenol-co-methyl methacrylate.

By the choice of the crosslinking component and the concentration thereof in the polymer formulation, the
15 mechanical properties of the polymer layer and the resistance to chemicals can be decisively controlled.

By the choice of the photo acid generator, wavelength and exposure dose for the initiation of the
20 crosslinking reaction can be controlled. The temperature of the post exposure bake (PEB) determines the duration of the crosslinking step since this is determined substantially by the diffusion of the photo generated acid.

25 The choice of the solvent determines the film formation properties of the formulation.

Two polymer formulations which differ only in the
30 proportion of the crosslinking agent are described below as examples.

Formulation 1 is a 10% strength solution in propylene glycol monomethyl ether acetate (PGMEA). 100 parts of
35 base polymer, 10 parts of crosslinking agent and 2.5 parts of photo acid generator are present.

A mixture of 2 g of PVP (MW about 20 000) as base polymer and 200 mg of 4-hydroxymethylbenzyl alcohol as crosslinking agent are dissolved in 20.5 g of PGMEA as solvent on a shaking apparatus (about 3 hours).

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Thereafter, 50 mg of triphenylsulfonium hexaflate as a photo acid generator are added and the total solution is shaken for a further hour. Before use, the polymer solution is filtered through a 0.2 μ m filter.

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Formulation 2 is a 10% strength solution in PGMEA. 100 parts of base polymer, 20 parts of crosslinking agent and 2.5 parts of photo acid generator are present. The proportion of crosslinking agent is therefore twice as high as in the formulation 1.

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A mixture of 2 g of PVP (MW about 20 000) as base polymer and 400 mg of 4-hydroxymethylbenzyl alcohol as crosslinking agent are dissolved in 20.5 g of PGMEA as solvent on a shaking apparatus (about 3 hours). Thereafter, 50 mg of triphenylsulfonium hexaflate as a photo acid generator are added and the total solution is shaken for a further hour. Before use, the polymer solution is filtered through a 0.2 μ m filter.

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Film preparation:

2 ml of the formulation 1 were applied by means of a spin coater at 4000 rpm for 22 s to a prepared substrate (PEN (polyethylene naphthalate) having Ti gate structures). Thereafter, drying is effected at 100°C for 2 min on a hotplate. The layer is then exposed (wavelength 365 nm, duration 30 seconds), intensity of irradiation 7 mW/cm²).

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A post exposure bake is then effected at 140°C in an oven under a 400 mbar N₂ atmosphere for 20 minutes.

The film preparation for formulation 2 is effected analogously.

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Structuring of the gate dielectric layer:

The structuring is effected as stated in the examples, except that the crosslinked polymer layer (gate dielectric layer 3) is exposed using a bright field chromium mask (chrome on glass COG). After the post exposure bake step, uncrosslinked dielectric (i.e. parts of the dielectric layer 3 which were not exposed to light) is dissolved away with acetone. The structured dielectric layer 3 remains in the exposed parts.

The source-drain layer 4a, 4b is then deposited and structured by standard methods (30 nm Au applied thermally by vapor deposition, photolithographic structuring and wet chemical etching with I₂/KI solution).

The layer thickness of the gate dielectric layers 2 is 200 nm for formulation 1. The roughness of the layer is 0.7 nm on 50 μ m.

The layer thickness of the gate dielectric layers is 210 nm for formulation 2. The roughness of the layer is 0.7 nm on 50 μ m.

The transistors or circuits are completed by applying the active component 5 (in this case pentacene) thermally by vapor deposition. Except for the passivating layer 6, the structure of an OFET according to fig. 1 is thus produced.

Here, embodiments for a polymer formulation and the use thereof for the production of gate dielectric layers 3 at low temperatures for use in integrated circuits based on OFETs are described. These gate dielectric layers 3 are distinguished by outstanding thermal, chemical, mechanical and electrical properties in addition to the low process temperature for the production thereof.

Fig. 3a shows a family of output characteristics of a pentacene OFET comprising an electrophilically crosslinked gate dielectric. Fig. 3b shows, for the same structure, the transmission characteristics of an OFET ($\mu = 0.8 \text{ cm}^2/\text{Vs}$, on/off ratio = 10^5). In fig. 4, a trace of an oscilloscope diagram is reproduced. The characteristic of a 5-stage ring oscillator is shown, the ring oscillator operating with a signal lag of 80 μsec per stage.

In connection with the figures, an OFET was used as the integrated circuit in an embodiment. In principle, the integrated circuit according to the invention can, however, also have a different structure in which a dielectric layer is used.

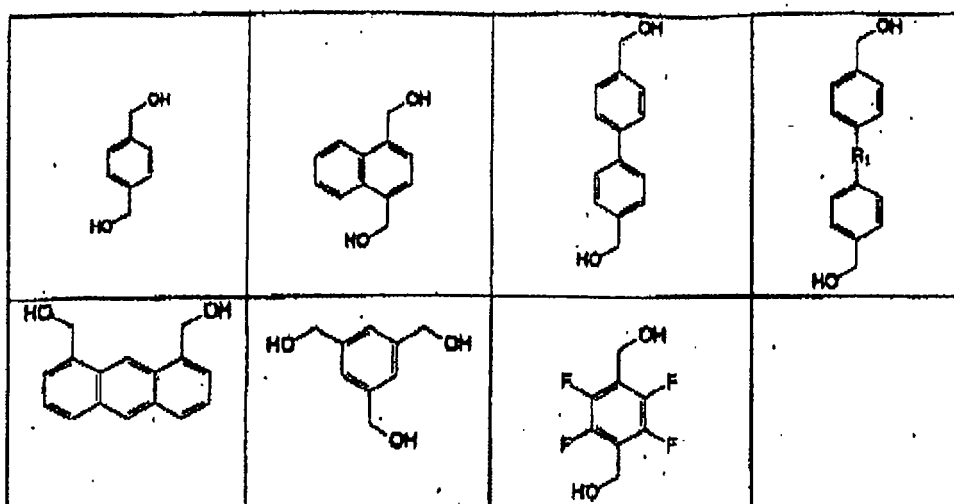
The invention is not limited in its execution to the abovementioned preferred embodiments. Rather, a number of variants which make use of the apparatus according to the invention and the method according to the invention also in versions of fundamentally different types is conceivable.

List of reference numerals

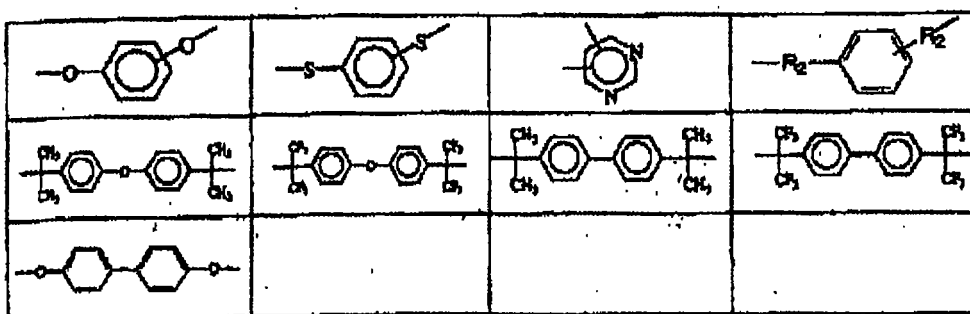
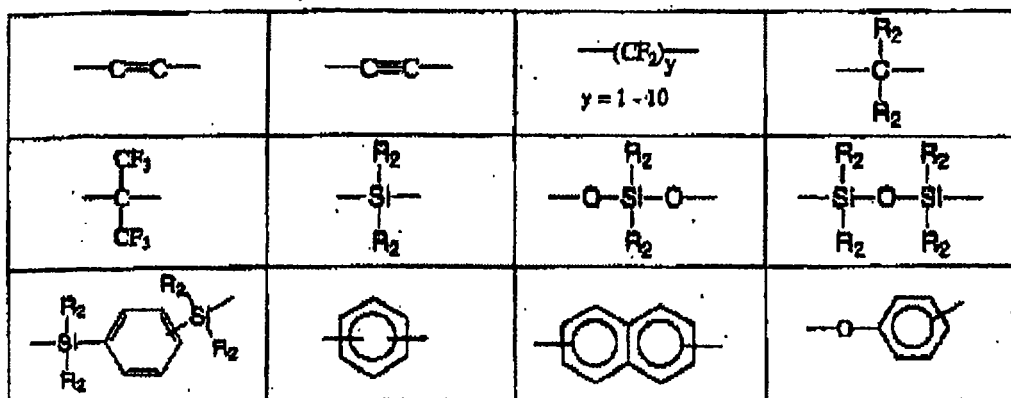
	1	Substrate
	2	Gate electrode
5	3	Gate dielectric layer
	4a	Drain layer
	4b	Source layer
	5	Active layer
	6	Passivating layer
10	7	Interconnect layer

Patent claims

1. An integrated circuit comprising an organic semiconductor, in particular an organic field effect transistor (OEFT), having a dielectric layer,
which can be produced by
a polymer formulation consisting of
 - a) 100 parts of at least one crosslinkable base polymer,
 - b) from 10 to 20 parts of at least one di- or tribenzyl alcohol compound as an electrophilic crosslinking component,
 - c) from 0.2 to 10 parts of at least one photo acid generator dissolved in
 - d) at least one solvent.
2. The integrated circuit as claimed in claim 1, characterized in that at least one base polymer is a phenol-containing polymer or copolymer, in particular poly-4-vinylphenol, poly-4-vinylphenol-co-2-hydroxyethyl methacrylate or poly-4-vinylphenol-co-methyl methacrylate.
3. The integrated circuit as claimed in claim 1 or 2, characterized in that at least one di- or tribenzyl alcohol compound as an electrophilic crosslinking component is 4-hydroxymethylbenzyl alcohol.
4. The integrated circuit as claimed in at least one of the preceding claims, characterized in that at least one crosslinking component has the following structures:



The following is true for R_1 : $-O-$, $-S-$, $-SO_2-$, $-S_x-$, $-(CH_2)_x-$, in which $x = 1 - 10$, and additionally:



The following is true for R_2 : alkyl having 1 to 10 carbon atoms or aryl

5. The integrated circuit as claimed in at least one of the preceding claims, characterized in that at least one photo acid generator is a compound which, on exposure to UV light, generates a photo acid for transferring a proton to the hydroxyl group of a benzyl alcohol.
6. The integrated circuit as claimed in claim 5, characterized in that at least one photo acid generator is a sulfonium or an iodonium salt, in particular triphenylsulfonium hexaflate.
7. The integrated circuit as claimed in at least one of the preceding claims, characterized in that at least one solvent is an alcohol, in particular n-butanol, propylene glycol monomethyl ether acetate (PGMEA), dioxane, N-methylpyrrolidone (NMP), γ -butyrolactone, xylene or a mixture.
8. The integrated circuit as claimed in at least one of the preceding claims, characterized by a proportion of base polymer, crosslinking component and photo acid generator of from 5 to 20% by mass.
9. A method for producing an integrated circuit comprising an organic semiconductor, in particular an OEFT having a dielectric layer, characterized in that
 - a) a polymer formulation as claimed in claim 1 is applied to a substrate (1), in particular having a prestructured gate electrode (2), and then
 - b) a photoinduced crosslinking reaction for the formation of crosslinked parts of the gate dielectric layer (3) is effected.

10. The method as claimed in claim 9, characterized in that the photoinduced crosslinking reaction is initiated by exposure to UV radiation.
11. The method as claimed in claim 9 or 10, characterized in that, after the exposure to light, a heating step, in particular a post exposure bake step, is effected.
12. The method as claimed in claim 11, characterized in that the temperature in the heating step is not more than 140°C, in particular 100°C.
13. The method as claimed in at least one of claims 9 to 12, characterized in that, after the post exposure bake (PEB), at least one further structuring for producing the OFET is effected.
14. The method as claimed in at least one of claims 9 to 13, characterized in that the polymer formulation is applied by spin coating, printing or spraying.
15. The method as claimed in at least one of claims 9 to 14, characterized in that the crosslinking reaction is effected under an inert gas atmosphere, in particular an N₂ atmosphere.
16. The method as claimed in at least one of claims 9 to 15, characterized in that, after the application of a polymer formulation, drying is effected, in particular at 100°C.
17. The method as claimed in at least one of claims 9 to 16, characterized in that

a source-drain layer (4a, 4b) is applied to the gate dielectric layer (3).

18. The method as claimed in at least one of claims 9 to 17, characterized in that an active layer (5) for the formation of an OFET, in particular comprising pentacene, is applied to the source-drain layer (4a, 4b).
19. The method as claimed in at least one of claims 9 to 18, characterized in that a passivating layer (6) is arranged on the active layer (5).