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(54) A stamp for soft lithography, in particular micro contact printing and a method of preparing the same

Stempel für die sanfte Lithographie, insbesondere für das Mikro-Kontaktdruckverfahren und Verfahren zu seiner Herstellung

Tampon pour la lithographie douce, en particulier pour le procede d'impression par microcontact et procede de sa fabrication

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EP 1 657 070 B1

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Description

[0001] The present invention relates to a stamp for soft lithography. It also relates to a method of preparing a stamp for soft lithography, in particular micro contact printing, and to uses of such stamp.

[0002] From the many micro fabrication techniques available, soft lithography has become a method of first choice in many laboratories for defining chemically micro- and nanostructured surfaces (Xia, Y; Whitesides, G.M.; Annu. Rev. Mater. Sci. 28 (1998), 153-184; Michel, B. et al.; IBM J. Res. & Dev. 45 (2001), 697 - 719). All different techniques summarised under the term "soft lithography" share the common feature of using a patterned elastomer as the stamp, mould or mask to generate micro- and nanopatterns and - structures. These various members include microcontact printing (μCP), replica moulding, micro transfer moulding, micro moulding in capillaries, solvent-assisted micro moulding, phase-shift photolithography, cast moulding, embossing and injection moulding. A review of various soft lithography techniques can be found in Xia et al., 1998, Annu. Rev. Mater Sci., 28:153-184. Among these soft lithography techniques, the technique of microcontact printing has become the most commonly used method (Xia et al., ibid). Here, an "ink" of molecules is spread on a patterned polymer stamp surface. Subsequently the stamp is brought into contact with a substrate. At this point, the molecules are transferred to the surface of the substrate where they ideally form self assembled mono layers (Delamarche, E. et al.; J. Phys. Chem. B 102 (1998), 3324-3334; Delamarche, E. et al.; J. Am. Chem. Soc. 124 (2002), 3834-3835). Microcontact printing commonly uses stamps of for example poly(dimethylsiloxane) (commercially available for example as Sylgard 184 PDMS). However, this polymer having a Young's modulus of 3MPa proved to be too soft to define feature sizes below 500 nm (Michel, B. et al.; IBM J. Res. & Dev. 45 (2001), 697-719).

[0003] Stamp materials in soft lithography are subjected to self-adhesion and mechanical stresses during printing. These stresses during printing can cause the material to deform (Schmid, H.; Michel, B.; Macromolecules 33 (2000), 3042-3049) or to collapse (Delamarche, E. et al.; Adv. Mater. 9 (1997), 741-746). In order to avoid the problems of deformation and collapsing due to the material properties of the soft Sylgard 184, new polymeric materials have been tested for their suitability for μCP purposes. The most promising approach is a composite polymeric stamp consisting of a thick flexible PDMS 184 slab and a thin and hard PDMS layer with the designed structure (Schmid, H.; Michel, B.; Macromolecules 33 (2000), 3042-3049; Odom, T. W. et al.; Langmuir 18 (2002), 5314-5320). The hard PDMS consists of a mixture of vinyl PDMS prepolymer, a platinum divinyltetramethyldisiloxane catalyst, a tetramethyl tetravinyl cyclotetrasiloxane modulator and a hydrosilane prepolymer. The resulting polymer has a Young's modulus of 9.7 MPa. Structures with feature sizes of 50 nm were achieved using the composite stamps (Odom, T. W. et al.; J. Am. Chem. Soc. 124 (2002), 12112-12113).

[0004] There are different attempts using non-PDMS materials with high Young's modulus like block copolymer thermoplastic elastomers (Trimbach, D. et al.; Langmuir 19 (2003), 10957-10961) and polyolefin plastomers (Csucs, G. et al.; Langmuir 19 (2003), 6104-6109). In the first case, structures down to 1 μm could be realized. Using the polyolefin plastomers, structure sizes down to 100 nm were achieved.

[0005] Choi and Rogers (Journal of the American Chemical Society, No. 125, 2003, pages 4060 - 4061) disclose poly(dimethylsiloxane) which is photocurable and its use in soft lithographic applications on the nanometre scale.

[0006] EP 1193056 A1 discloses a silicone elastomer stamp with hydrophilic surfaces and its use in micro-contact printing.

[0007] The material commonly used in micro contact printing so far are either too soft for creating reliable prints below a feature size <200 nm, or the stamps, especially the more highly resolving composite polymeric stamps are difficult to fabricate.

[0008] Accordingly, it was an object of the present invention to provide for a method of preparing a stamp which is easy to perform and which allows the fabrication of stamps at least as good in terms of resolution as the ones from the prior art. Furthermore it was an object of the present invention to provide for a stamp allowing micro contact printing with a resolution < 500 nm, which stamp is easy to fabricate and therefore cheap in manufacture.

[0009] All these objects are solved by a stamp for soft lithography, in particular for micro contact printing, characterized in that it is made of an ionomeric polymer.

[0010] In one embodiment, said ionomeric polymer is poly(ethylene-co-methacrylic acid), wherein, preferably, said poly(ethylene-co-methacrylic acid) is a polymer wherein ethylene has been randomly copolymerized with methacrylic acid at a ratio of 10:1 to 100:1, preferably > 10.

[0011] Preferably, said poly(ethylene-co-methacrylic acid) has a mean molecular weight in the range of from 50,000 to 200,000, preferably 100,000 - 150,000.

[0012] More preferably, said poly(ethylene-co-methacrylic acid) some or all of the methacrylic acid carboxyl groups are in the form of zinc carboxylate or sodium carboxylate.

[0013] In one embodiment, said stamp has a Young's modulus >20 MPa.

[0014] Preferably, said stamp further comprises a cured silicone-based material, wherein, preferably, it comprises a first part for printing, said first part being made of said ionomeric polymer, and a second part for providing conformal contact of the stamp with a substrate surface to be printed on, said second part being made of said cured silicone-based material.

[0015] In one embodiment, said cured silicone-based material is a polydimethylsiloxane polymer, preferably a vinyl-polydimethylsiloxane polymer.

[0016] Preferably, said first part has a front face for printing and a back face opposite said front face, and said second part is arranged on said back face of said first part such that said first part is at least partially embedded in said second part, wherein, more preferably, said second part provides a margin extending beyond said first part, preferably all around said first part, said margin allowing for conformal contact with a surface to be printed on.

[0017] In a preferred embodiment, said front face has a structured surface for printing.

[0018] The objects of the present invention are also solved by a method of preparing a stamp for soft lithography, in particular for microcontact printing, comprising the steps:

(a) providing a master having a surface and a relief structure on said surface,
(b) providing a polymeric foil,
(c) pressing said master into said polymeric foil thus leaving an imprint of said relief structure on said polymeric foil,
(d) releasing said master from said imprinted polymeric foil, said polymeric foil being made of an ionomeric polymer, preferably poly(ethylene-co-methacrylic acid).

[0019] In a preferred embodiment step d) occurs in the presence of a release agent, e.g. a fluorinated silane.

[0020] In a preferred embodiment, step c) occurs for a time in the range of from 1 min to 120 min, preferably 10 min to 60 min, more preferably 30 min to 60 min, and most preferably > 40 min.

[0021] In one embodiment, step c) occurs with a pressure in the range of from 100 kPa to 250 kPa, preferably 150 kPa to 200 kPa.

[0022] Prefereby, step c) occurs at an elevated temperature in the range of from 80°C to 150°C, preferably 100°C to 135°C, more preferably 120°C to 130°C, most preferably around 125°C.

[0023] In one embodiment, said master or said polymeric foil or both are kept at said elevated temperature during step c).

[0024] In a preferred embodiment, step d) occurs after cooling down to room temperature.

[0025] Preferably, said polymeric foil has a thickness in the range of from 50 μm to 500 μm, preferably 75 μm to 300 μm, more preferably 100 μm to 200 μm, most preferably around 150 μm.

[0026] In one embodiment, said poly(ethylene-co-methacrylic acid) is a polymer wherein ethylene has been randomly copolymerised with methacrylic acid at a ratio of 10:1 to 100:1, preferably > 10.

[0027] Preferably, said poly(ethylene-co-methacrylic acid) has a mean molecular weight in the range of from 50000 to 200000, preferably 100000 - 150000.

[0028] More preferably, in said poly(ethylene-co-methacrylic acid) some or all of the methacrylic acid carboxyl groups are in the form of zinc carboxylate or sodium carboxylate.

[0029] In one embodiment, said foil is made of a material capable of achieving a Young's modulus > 20 MPa after heating.

[0030] In one embodiment, said imprinted polymeric foil has a front face for printing and a back face opposite said front face, and after step d) a curable silicone-based material is placed on said back face of said imprinted polymeric foil and subsequently cured, said imprinted polymeric foil thus being at least partially embedded in said cured silicone-based material, wherein preferably, said front face has a structured surface for printing.

[0031] In one embodiment, said curable silicone-based material is a polydimethylsiloxane prepolymer, preferably a vinyl-polydimethylsiloxane prepolymer and is cured in the presence of a catalyst, preferably a platinum catalyst, and of copolymers of methylhydrosiloxane and dimethylsiloxane.

[0032] Preferably, after step d) a surface, preferably said front face of said imprinted polymeric foil is further modified, wherein, preferably, said surface is further modified by a process selected from plasma treatment, chemical modification and treatment with a surfactant.

[0033] It should be noted that such surface modification has the purpose of lowering ink adhesion to the surface for an easy transfer process.

[0034] The objects of the present invention are also solved by a stamp produced by the method according to the present invention.

[0035] The objects of the present invention are also solved by the use of a stamp according to the present invention for soft lithography, in particular microcontact printing, wherein, preferably, said stamp is inked by contact inking or wet inking.

[0036] Preferably, said use is for microcontact printing of conducting leads or paths, preferably of grid-structures or cross-bar structures. In particular said use is for microcontact printing of conducting leads or paths, preferably of conducting leads or paths which cross each other and/or intersect with each other (crossing conducting leads/paths or intersecting conducting leads/paths).

[0037] Preferably, said grid-structures and/or said cross-bar structures are structures made of conducting leads, more preferably having a width in the range of from 10 nm to 200 nm. In one embodiment, said grid-structures and/or said cross-bar structures comprise pads, preferably having an edge length of about 100 μm.

[0038] Such conducting paths or leads may, for example, be realised by printing a structure using an inorganic ink, e.g. a metal, with line widths in the range of from 10 nm to 100 μm, preferably 10 nm to 200 nm. In another embodiment, also pads may be printed having an edge length of about 100 μm.

[0039] As used herein, the term "cross-bar-structures"

is meant to signify any structure
wherein printed features, like lines, cross each other.

[0040] The objects of the present invention are also solved by a method of microcontact printing, comprising the steps:

e) providing a stamp according to the present invention,
f) inking said stamp, preferably by contact inking or wet inking,
g) pressing said inked stamp on a substrate.

[0041] The objects of the present invention are also solved by the use of an ionomeric polymeric material, as defined above, for soft lithography, in particular microcontact printing.

[0042] The inventors have surprisingly found that an ionomeric polymer, in particular poly-(ethylene-co-methacrylic acid) allows for the fabrication of stamps particularly suited for micro contact printing. More specifically, a combination of the technique of hot embossing and the use of a polymeric ionomeric foil allows for the production of high quality stamps to be used in micro contact printing. The stamps thus produced can achieve a high aspect ratio, e.g. > 2.0. In particular, it has been found out that an ionomeric polymeric foil appears to be particularly useful for that purpose. The stamps are cheap and easy to manufacture. Without wishing to be bound by any theory it is believed that in an ionomeric polymer, the polymer structure has three regions, namely amorphous polymer, crystalline polymer and ionic clusters. It appears as if these features are responsible for the superior abrasion resistance, thermoplasticity and the higher hardness. One example that appears to be particularly useful for that purpose is a poly(ethylene-co-methacrylic) copolymer, e.g. commercially available from DuPont as Surlyn®. Surlyn® is a commercial thermoplastic ionomeric resin that was introduced by DuPont in the early nineteen sixties. Its commercial applications are within the packaging industry. Some of the properties that make Surlyn® excellent for such packaging applications are its sealing performance, formability, clarity, oil/grease resistance and high hot draw strength. Good hot draw strength allows for a faster packaging line speed and reduces packaging failures. Another well known application of Surlyn® is its use in the outer covering of golf balls. To the best of the inventors' knowledge, Surlyn®, or other ionomeric polymers have not been used for the fabrication of stamps for micro contact printing. In Surlyn® some of carboxyl groups of the methacrylic acid part are in the form of zinc carboxylate and/or sodium carboxylate.

[0043] The combination of a polymeric ionomeric foil with hot embossing technique is simple and thus amenable to processing on an industrial scale, for example in roll-to-roll-manufacturing processes.

[0044] Fabrication of a master to be used for imprinting on the polymeric foil according to the present invention is a process known to someone skilled in the art and has for example been described in Xia et al., ibid. For example, the master may be fabricated using micro lithographic techniques such as photo lithography, micro machining, electron-beam-writing or from available relief structures such as diffraction gratings, TEM grids, polymer beads assembled on solid supports and relief structures etched in metals or Si.

[0045] The process of micro contact printing itself has in detail been described in Xia et al., ibid. and Michel et al. ibid. and is therefore well known to someone skilled in the art.

[0046] Using the method and the stamp according to the present invention, a cheap way of producing micro contact printing stamps is provided by which structures of a resolution < 100 nm can easily be realised.

[0047] Furthermore, the inventors have surprisingly found that the invention allows for the fabrication of composite stamps comprising a first part for the actual printing process, and a second part into which the first part for printing is at least partially embedded, which second part allows for a conformal contact of the stamp with a substrate surface to be printed on. According to the invention, the first part is made of the ionomeric polymer, whereas the second part is made of a soft polymer, preferably a polydimethylsiloxane polymer which provides for a strong adhesion of the stamp according to the present invention to a substrate surface to be printed on. The second part or "soft polymer" part is arranged on the back of the first part (or "ionomeric polymer part"), and preferably extends over the edges of said first part, thus providing a margin all around the first part. As used herein, the term "the first part is at least partially embedded in said second part" is meant to mean that the back face of said first part is covered by said second part, whereas the front face of said first part is fully accessible and can be used for the actual printing progress.

[0048] As used herein, the term "ionomeric polymer" is meant to signify a copolymer having a proportion of hydrophobic monomers and another proportion of comonomers, which comonomers carry ionic groups. These ionic groups may be present in the main chain (back bone) of the polymer but also in side chains of the polymer. Preferably, the proportion of hydrophobic monomers is larger than the proportion of the comonomers carrying the ionic groups. In a preferred embodiment, the proportion of comonomers carrying ionic groups may be as high as 15%.

[0049] In the following reference is made to the figures wherein

figure 1 shows a conventional stamp according to the prior art using Sylgard™ 184 PDMS, having bar structures ranging from a bar width of 200 nm to 2 μm,

figure 2 shows an optical microscope picture of a patterned Surlyn™ stamp surface (a), and a picture of the same surface taken with the scanning electron microscope (b),

figure 3 shows a thiol structure transferred by a Surlyn® stamp according to the present invention under finger pressure to an Au surface (a) and figure 3b shows another transferred thiol test structure,

figure 4 shows an approximately 20 nm thick Au electrode structure printed with a stamp according to the present invention,

figure 5 shows a thiol structure transferred under soft pressure provided by a composite Surlyn®/PDMS stamp according to the present invention, and

figure 6 shows the principle of a composite stamp according to the present invention showing a soft polymer cushion (grey) encompassing a structured hard polymeric foil (black) which is the part actually used for printing.

[0050] In the following reference is made to the examples which are given to illustrate, not to limit the invention.

Example 1

Master replication

[0051] Surlyn® is a hard polymer with a Young's modulus above 20 MPa. This polymer is used as one example of a polymer useful for the present invention. The replication of structures into this material is realized with hot embossing technique using a thin Surlyn® foil with a thickness of ≈ 150 μm. For the fabrication of stamps, a SiO_2 master (fabricated by e-beam lithography and subsequent RIE etching) and the Surlyn® foil are placed between two SDS (sodium dodecyl sulfate) covered glass plates and the master is pressed at a temperature of 125 ˚C into the foil. Processs times around 10 min appeared to be reasonable for an almost complete pattern replication. However, an increase to 40 min results in a significant replication improvement. After cooling down to room temperature and separation of the stamp from the master, a complete pattern transfer with the same height as the master pattern can be obeserved. At 120 ˚C Surlyn® partly forms a network resulting in an increase in hardness. The Young's modulus was measured to be above 20 MPa. Figure 2 a) and b) show an optical microscope and a SEM picture of the smooth and almost defect free stamp surface.

Example 2

Printing with stamps made of ionomeric resins, e.g. Surlyn®

a) Printing of molecules

[0052] Using Surlyn® as an example, ionomeric resins prove to be suitable materials for μCP. Printing experiments have been made using octadecanethiols as material to be transferred. The stamp has been inked using the method of contact and wet inking. For contact inking, the stamp is placed for 2 minutes on a piece of PDMS which was exposed to a 10^{-3} M thiol solution (in ethanol) over night and dried afterwards. Alternatively, in case of wet inking, the stamp is covered by a small amount of the molecule solution (10^{-3} M) which is dropped directly on the stamp and dried after 30 s with a stream of nitrogen. Subsequently, the stamp is brought into contact with an Au substrate. Finger pressure was applied for 5 minutes in order to obtain conformal contact between the stamp and the substrate. Figure 3 a) and b) shows SEM images of the transferred pattern using a stamp that was inked with the contact inking method and pressed with the finger against the Au substrate. The structured area was completely transferred. In addition, unspecific transfer of molecules due to a certain sagging effect can be observed, i.e. unwanted areas of the stamp surface were also in contact with the substrate. Up to the moment, printing of smaller structures down to 100 nm have been successfully realized using Surlyn® with its high Young's modulus as stamp material (Figure 3b).

b) Printing of Gold

[0053] Printing of Au electrodes on top of modified substrate surfaces is a further requirement Surlyn® proved to be suitable for.

i) Printing Au on Au substrate

[0054] Approximately 20 nm of Au were freshly thermally evaporated onto an unmodified Surlyn stamp surface. The stamp was subsequently pressed for 15 hours on a nonanedithiol covered Au substrate. The thiol group serves as anchor point for the printed electrodes (one thiol group binds to the Au substrate while the second thiol group binds to the Au top-electrode). After the stamp was removed, a clear Au transfer to the molecule covered Au surface could be observed (Fig. 4). According to the SEM image of the stamped electrodes (Fig. 4), the Au layer is not uniform, i.e. the structure consists of a high amount of Au islands. Compared to the Au structures printed with Surlyn (contact angle ≈ 95˚), the Au structures stamped with PDMS (contact angle ≈ 105˚) appear flat and uniform without island formation.
Up to the moment it is unclear whether this island formation happens on the stamp surface before the transfer or during the transfer on the substrate. However, it is expected that a uniform Au electrode structure can be achieved by simply using either thicker (≈ 50nm) Au lay-

ers on the stamp or by modifying the Surlyn surface. After e.g. plasma treatment, Surlyn contains surface OH groups that can be used for the attachment of molecules with terminal groups that can alter the hydrophilicity of the surface. More hydrophyilic surfaces lead to continous and smooth Au films on the polymer surface.

ii) Printing Au on SiO_2 substrate

[0055] As a modification, printing of Au is also possible on SiO_2 surfaces functionalized with Aminosilanes or Mercaptosilanes, i.e. Trimethoxysilylpropylethylendiamin or Mercaptopropyltriethoxysilan, respectively.
In this case, the Si atom of the silane binds via an O-bridge to the substrate surface while the Amino- or the mercapto group serves as anchor point to the printed Au electrode. Prerquisite for this process is that the SiO_2 surface is homogenously covered with the required functional group.

iii) Lubricant for transfer of Au

[0056] Critical for the successful transfer of Au onto SiO_2 surfaces are the interaction forces at the interfaces between stamp/Au andAu/modified SiO_2 surface. Strong adhesion between Au and the Surlyn stamp inhibits the Au transfer. A lubricant film between the Au layer and the Surlyn surface can reduce the adhesion force and therefore provide a complete and unproblematic transfer process. Fluorosilanes could serve as lubricants since they bind via carboxyl groups to the polymer surface which carboxyl groups are located at the polymer surface. The F-atom minimizes because of its high hydrophobicity the adhesion of the Au film to the stamp. Before evaporation of Au on the stamp, its surface has to be modified with the appropriate fluorosilane. The fluorosilanisation process can be done in either vacuum via the gas phase or in solution. In both cases an activation of the stamp surface with OH groups is necessary in order to provide anchor point for the molecules on the Polymer surface.

Example 3

Composite stamps

[0057] Another critical parameter for the pattern transfer is the contact between the stamps and the surface. Conventionally, the stamp is pressed onto the surface in order to achieve conformal contact between the stamp and the substrate. Composite stamps have been proposed and described in the past for two different kinds of PDMS. They consist of a thick flexible PDMS 184 slab and a thin and hard PDMS layer with the designed structure (Schmid, H.; Michel, B.; Macromolecules 33 (2000), 3042-3049; Odom, T. W. et al.; Langmuir 18 (2002), 5314-5320). The hard PDMS contains of a mixture of vinyl PDMS prepolymer, a platinumdivinyltetramethyldisiloxane catalyst, a tetramethyltetravinylcyclotetrasiloxane modulator and a hydrosilane prepolymer. The resulting polymer has a Young's modulus of 9.7 MPa. Structures with feature sizes of 50 nm were achieved using the composite stamps (Odom, T. W. et al.; J. Am. Chem. Soc. 124 (2002), 12112-12113).

[0058] According to one aspect of the present invention, composite two layer stamps containing ionomeric resins, e.g. Surlyn are envisaged as a possible solution to overcome the problem of the low adhesion force of the ionomeric, e.g. Surlyn material on one side and a sagging effect by applying pressure on the other side, i.e. use of two-layer stamps. These composite stamps consist of a thin (≈ 150 μm) Surlyn layer containing the actual stamp pattern and a thicker (≈ 2 mm) second PDMS layer. The PDMS layer is poured as a liquid on top of the Surlyn backside and subsequently cured. This second PDMS layer guarantees a conformal contact of the stamp surface to the substrate surface. By its body weight and its property to suck itself onto the surface, the PDMS layer presses the Surlyn layer softly on the substrate and balances all unevenness of a surface in parallel. In order to amplify this effect, the PDMS layer could be larger than the Surlyn film resulting in a direct contact between PDMS and the substrate material at the Surlyn edges. Since PDMS has the property to suck itself to the surface, the stamp should be pressed softly to conformal contact. The soft pressure due to adhesion of the PDMS avoids the sagging effect (Fig. 5). Thus, composite stamps according to the present invention consist of a thin structured hard polymeric ionomeric foil, e.g. Surlyn ™ foil, and a soft polymer cushion (preferably PDMS) with overlapping margin. The advantage of using a soft polymeric material on top of the polymeric foil is to provide a flexible stamp backbone. The weight of the thicker soft polymer back and especially the adhesion force between the margin and the substrate enables conformal contact of the structured polymer foil with the substrate surface and provides the appropriate pressure for the printing process.

[0059] The features disclosed in the specification, the claims and/or in the accompanying drawings, may, both separately, and in any combination thereof, be material for realising the invention in various forms thereof.

Claims

1. A stamp for soft lithography, in particular for micro contact printing, **characterized in that** it is made of an ionomeric polymer.

2. The stamp according to claim 1, **characterized in that** said ionomeric polymer is poly(ethylene-co-methacrylic acid).

3. The stamp according to claim 2, wherein said poly (ethylene-co-methacrylic acid) is a polymer wherein

ethylene has been randomly copolymerized with methacrylic acid at a ratio of 10:1 to 100:1, preferably > 10.

4. The stamp according to any of claims 2 - 3, wherein said poly(ethylene-co-methacrylic acid) has a mean molecular weight in the range of from 50,000 to 200,000, preferably 100,000 - 150,000.

5. The stamp according to any of claims 2 - 4, wherein in said poly(ethylene-co-methacrylic acid) some or all of the methacrylic acid carboxyl groups are in the form of zinc carboxylate or sodium carboxylate.

6. The stamp according to any of the foregoing claims, **characterized in that** it has a Young's modulus >20 MPa.

7. The stamp according to any of the foregoing claims, further comprising a cured silicone-based material.

8. The stamp according to claim 7, comprising a first part for printing, said first part being made of said ionomeric polymer, and a second part for providing conformal contact of the stamp with a substrate surface to be printed on, said second part being made of said cured silicone-based material.

9. The stamp according to any of claims 7 - 8, wherein said cured silicone-based material is a polydimethylsiloxane polymer, preferably a vinyl-polydimethylsiloxane polymer.

10. The stamp according to any of claims 8 - 9, **characterized in that** said first part has a front face for printing and a back face opposite said front face, and said second part is arranged on said back face of said first part such that said first part is at least partially embedded in said second part.

11. The stamp according to claim 10, **characterized in that** said second part provides a margin extending beyond said first part, preferably all around said first part, said margin allowing for conformal contact with a surface to be printed on.

12. The stamp according to any of claims 10 - 11, **characterized in that** said front face has a structured surface for printing.

13. A method of preparing a stamp for soft lithography, in particular for microcontact printing, comprising the steps:

(a) providing a master having a surface and a relief structure on said surface,
(b) providing a polymeric foil,
(c) pressing said master into said polymeric foil thus leaving an imprint of said relief structure on said polymeric foil,
(d) releasing said master from said imprinted polymeric foil, said polymeric foil being made of an ionomeric polymer, preferably poly(ethylene-co-methacrylic acid).

14. The method according to claim 13, wherein step c) occurs at an elevated temperature in the range of from 80˚C to 150˚C, preferably 100˚C to 135˚C, more preferably 120˚C to 130˚C, most preferably around 125˚C.

15. The method according to claim 14, wherein said master or said polymeric foil or both are kept at said elevated temperature during step c).

16. The method according to any of claims 13 - 15, wherein said poly(ethylene-co-methacrylic acid) is a polymer wherein ethylene has been randomly copolymerised with methacrylic acid at a ratio of 10:1 to 100:1, preferably > 10.

17. The method according to any of claims 13 - 16 , wherein said poly(ethylene-co-methacrylic acid) has a mean molecular weight in the range of from 50000 to 200000, preferably 100000 - 150000.

18. The method according to any of claims 13 - 17, wherein in said poly(ethylene-co-methacrylic acid) some or all of the methacrylic acid carboxyl groups are in the form of zinc carboxylate or sodium carboxylate.

19. The method according to any of claims 13-18, wherein said foil is made of a material capable of achieving a Young's modulus > 20 MPa after heating.

20. The method according to any of claims 13 - 19, wherein said imprinted polymeric foil has a front face for printing and a back face opposite said front face, and after step d) a curable silicone-based material is placed on said back face of said imprinted polymeric foil and subsequently cured, said imprinted polymeric foil thus being at least partially embedded in said cured silicone-based material.

21. The method according to claim 20, wherein said front face has a structured surface for printing.

22. The method according to any of claims 20 - 21, wherein said curable silicone-based material is a polydimethylsiloxane prepolymer, preferably a vinyl-polydimethylsiloxane prepolymer and is cured in the presence of a catalyst, preferably a platinum catalyst, and of copolymers of methylhydrosiloxane and dimethylsiloxane.

23. The method according to any of the foregoing claims, wherein after step d) a surface, preferably said front face of said imprinted polymeric foil is further modified.

24. The method according to claim 23, wherein said surface is further modified by a process selected from plasma treatment, chemical modification and treatment with a surfactant.

25. A stamp produced by the method according to any of claims 13 - 24.

26. Use of a stamp according to any of claims 1 - 12 and 25 for soft lithography, in particular microcontact printing.

27. Use according to claim 26, wherein said stamp is inked by contact inking or wet inking.

28. Use according to any of claims 26 - 27 for microcontact printing of conducting leads or paths, in particular of grid-structures or cross-bar structures, wherein, preferably, said grid-structures and/or said cross-bar structures are structures made of conducting leads, more preferably having a width in the range of from 10 nm to 200 nm, and/or wherein, preferably, said grid-structures and/or said cross-bar structures comprise pads, more preferably having an edge length of about 100 μm.

29. A method of microcontact printing, comprising the steps:

e) providing a stamp according to any of claims 1 - 12 and 25,
f) inking said stamp, preferably by contact inking or wet inking,
g) pressing said inked stamp on a substrate.

30. Use of an ionomeric polymeric material, as defined in any of claims 1 - 6, in a stamp for soft lithography, in particular microcontact printing.

Patentansprüche

1. Stempel für die weiche Lithographie, insbesondere für das Mikro-Kontakt-Drucken ("micro contact printing"), **dadurch gekennzeichnet, dass** er aus einem ionomeren Polymer gemacht ist.

2. Stempel nach Anspruch 1, **dadurch gekennzeichnet, dass** das ionomere Polymer Poly(ethylen-co-methacrylsäure) ist

3. Stempel nach Anspruch 2, wobei die Poly(ethylen-co-methacrylsäure) ein Polymer ist, bei dem Ethylen mit Methacrylsäure in einem Verhältnis von 10:1 bis 100:1, bevorzugt > 10, statistisch copolymerisiert ist.

4. Stempel nach einem der Ansprüche 2-3, wobei die Poly(ethylen-co-methacrylsäure) ein mittleres Molekulargewicht im Bereich von 50000 bis 200000, bevorzugt 100000 - 150000 hat.

5. Stempel nach einem der Ansprüche 2-4, wobei in der Poly(ethylen-co-methacrylsäure) einige oder alle der Methacrylsäurecarboxylgruppen in der Form von Zinkcarboxylat oder Natriumcarboxylat sind.

6. Stempel nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** er ein Young'sches Modul > 20 MPa hat.

7. Stempel nach einem der vorangehenden Ansprüche, weiterhin umfassend ein ausgehärtetes Silicon-basierendes Material.

8. Stempel nach Anspruch 7, umfassend einen ersten Teil zum Drucken, wobei der erste Teil aus dem ionomeren Polymer gemacht ist, und einen zweiten Teil zum Bereitstellen eines konturgetreuen Kontakts ("conformal contact") des Stempels mit einer zu bedruckenden Substratoberfläche, wobei der zweite Teil aus dem ausgehärteten Silicon-basierenden Material gemacht ist.

9. Stempel nach einem der Ansprüche 7-8, wobei das ausgehärtete Silicon-basierende Material ein Polydimethylsiloxanpolymer, bevorzugt ein Vinyl-polydimethylsiloxanpolymer ist.

10. Stempel nach einem der Ansprüche 8-9, **dadurch gekennzeichnet, dass** der erste Teil eine Vorderseite zum Drucken und eine Rückseite gegenüber der Vorderseite hat, und dass der zweite Teil auf der Rückseite des ersten Teils so angeordnet ist, dass der erste Teil wenigstens teilweise in dem zweiten Teil eingebettet ist.

11. Stempel nach Anspruch 10, **dadurch gekennzeichnet, dass** der zweite Teil einen Rand bereitstellt, der sich über den ersten Teil, bevorzugt um den gesamten ersten Teil herum erstreckt, wobei der Rand einen konturgetreuen Kontakt mit einer zu bedruckenden Oberfläche ermöglicht.

12. Stempel nach einem der Ansprüche 10-11, **dadurch gekennzeichnet, dass** die Vorderseite eine strukturierte Oberfläche zum Drucken hat.

13. Verfahren zum Herstellen eines Stempels für die weiche Lithographie, insbesondere zum Mikro-Kontakt-Drucken, umfassend die Schritte:

(a) Bereitstellen eines Master ("master") mit einer Oberfläche und einer Reliefstruktur auf der Oberfläche,
(b) Bereitstellen einer Polymer-Folie,
(c) Drücken des Master in die Polymerfolie, wodurch eine Prägung der Reliefstruktur auf der Polymerfolie hinterlassen wird,
(d) Lösen des Master von der geprägten Polymerfolie, wobei die Polymerfolie aus einem ionomeren Polymer, bevorzugt aus Poly(ethylen-co-methacrylsäure) gemacht ist.

14. Verfahren nach Anspruch 13, wobei Schritt c) bei einer erhöhten Temperatur im Bereich von 80°C bis 150°C, bevorzugt 100°C bis 135°C, bevorzugter 120°C bis 130°C, am bevorzugtesten ungefähr 125°C, stattfindet.

15. Verfahren nach Anspruch 14, wobei der Master oder die Polymerfolie oder beide auf der erhöhten Temperatur während des Schrittes c) gehalten werden.

16. Verfahren nach einem der Ansprüche 13-15, wobei die Poly(ethylen-comethacrylsäure) ein Polymer ist, bei dem Ethylen mit Methacrylsäure in einem Verhältnis von 10:1 bis 100:1, bevorzugt > 10, statistisch copolymerisiert worden ist.

17. Verfahren nach einem der Ansprüche 13-16, wobei die Poly(ethylen-comethacrylsäure) ein mittleres Molekulargewicht im Bereich von 50000 bis 200000, bevorzugt 100000 - 150000 hat.

18. Verfahren nach einem der Ansprüche 13-17, wobei in der Poly(ethylen-comethacrylsäure) einige oder alle der Methacrylsäurecarboxylgruppen in der Form von Zinkcarboxylat oder Natriumcarboxylat sind.

19. Verfahren nach einem der Ansprüche 13-18, wobei die Folie aus einem Material gemacht ist, das in der Lage ist, einen Young'schen Modul > 20 MPa nach dem Erhitzen zu erzielen.

20. Verfahren nach einem der Ansprüche 13-19, wobei die geprägte Polymerfolie eine Vorderseite zum Drucken und eine Rückseite gegenüber der Vorderseite hat, und nach Schritt d) ein aushärtbares Silicon-basierendes Material auf die Rückseite der geprägten Polymerfolie gebracht und im Anschluß daran ausgehärtet wird, wobei die geprägte Polymerfolie so wenigstens teilweise in das ausgehärtete, Silicon-basierende Material eingebettet ist.

21. Verfahren nach Anspruch 20, wobei die Vorderseite eine strukturierte Oberfläche zum Drucken hat.

22. Verfahren nach einem der Ansprüche 20-21, wobei das aushärtbare, Silicon-basierende Material ein Polydimethylsiloxan-Präpolymer, bevorzugt ein Vinylpolydimethylsiloxan-Präpolymer ist und in der Anwesenheit eines Katalysators, bevorzugt eines Platin-Katalysators, und von Copolymeren aus Methylhydrosiloxan und Dimethylsiloxan ausgehärtet wird.

23. Verfahren nach einem der vorhergehenden Ansprüche, wobei nach Schritt d) eine Oberfläche, bevorzugt die Vorderseite der geprägten Polymerfolie weiter modifiziert wird.

24. Verfahren nach Anspruch 23, wobei die Oberfläche weiter modifiziert wird durch einen Prozeß, ausgewählt aus Plasma-Behandlung, chemischer Modifizierung und Behandlung mit einem oberflächenaktiven Mittel.

25. Stempel, hergestellt durch das Verfahren nach einem der Ansprüche 13-24.

26. Verwendung eines Stempels nach einem der Ansprüche 1-12 und 25 für die weiche Lithographie, insbesondere Mikro-Kontakt-Drucken.

27. Verwendung nach Anspruch 26, wobei der Stempel über ein Kontaktverfahren ("contact inking") oder ein Befeuchtungsverfahren ("wet inking") mit Tinte versehen wird.

28. Verwendung nach einem der Ansprüche 26-27 zum Mikro-Kontakt-Drucken von leitenden Leitungen oder Bahnen, insbesondere Gitterstrukturen oder Querbalken-Strukturen ("cross-bar structures"), wobei die Gitter-Strukturen und/oder die Querbalken-Strukturen Strukturen sind, die aus leitenden Bahnen gemacht sind, bevorzugter mit einer Breite im Bereich von 10 nm bis 200 nm, und/oder wobei , bevorzugt, die Gitterstrukturen und/oder die Querbalken-Strukturen Kissen ("pads") umfassen, bevorzugter mit einer Randlänge von ungefähr 100 μm.

29. Verfahren zum Mikro-Kontakt-Drucken, umfassend die Schritte:

(e) Bereitstellen eines Stempels nach einem der Ansprüche 1-12 und 25,
(f) Versehen des Stempels mit Tinte, bevorzugt mittels eines Kontaktverfahrens ("contact inking") oder eines Befeuchtungsverfahrens ("wet inking"),
(g) Drücken des mit Tinte versehenen Stempels auf ein Substrat.

30. Verwendung eines ionomeren polymeren Materials, wie in einem der Ansprüche 1-6 definiert, in einem Stempel für die weiche Lithographie, insbesondere Mikro-Kontakt-Drucken.

Revendications

1. Tampon pour lithographie douce, en particulier pour l'impression de microcontacts, **caractérisé en ce qu'**il est fait en un polymère ionomère.

2. Tampon selon la revendication 1, **caractérisé en ce que** ledit polymère ionomère est un copoly(éthylène/acide méthacrylique).

3. Tampon selon la revendication 2, dans lequel ledit copoly(éthylène/acide méthacrylique) est un polymère dans lequel l'éthylène a été soumis à une copolymérisation statistique avec l'acide méthacrylique en un rapport de 10/1 à 100/1, de préférence > 10.

4. Tampon selon l'une quelconque des revendications 2 et 3, dans lequel ledit copoly(éthylène/acide méthacrylique) a une masse moléculaire moyenne située dans la plage allant de 50 000 à 200 000, de préférence de 100 000 à 150 000.

5. Tampon selon l'une quelconque des revendications 2 à 4, dans lequel, dans ledit copoly (éthylène/acide méthacrylique), tout ou partie des groupes carboxyle d'acide méthacrylique est sous la forme de carboxylate de zinc ou de carboxylate de sodium.

6. Tampon selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**il a un module de Young > 20 MPa.

7. Tampon selon l'une quelconque des revendications précédentes, comprenant en outre un matériau siliconé durci.

8. Tampon selon la revendication 7, comprenant une première partie pour l'impression, ladite première partie étant faite en ledit polymère ionomère, et une deuxième partie pour permettre un contact conforme du tampon avec une surface de substrat sur laquelle doit être effectuée l'impression, ladite deuxième partie étant faite en ledit matériau siliconé durci.

9. Tampon selon l'une quelconque des revendications 7 et 8, dans lequel ledit matériau siliconé durci est un polymère de polydiméthylsiloxane, de préférence un polymère de vinyl-polydiméthylsiloxane.

10. Tampon selon l'une quelconque des revendications 8 et 9, **caractérisé en ce que** ladite première partie a une face recto pour l'impression et une face verso opposée à ladite face recto, et ladite deuxième partie est disposée sur ladite face verso de ladite première partie de façon que ladite première partie soit au moins partiellement encastrée dans ladite deuxième partie.

11. Tampon selon la revendication 10, **caractérisé en ce que** ladite deuxième partie constitue une lisière s'étendant au-delà de ladite première partie, de préférence tout autour de ladite première partie, ladite lisière permettant un contact conforme avec une surface sur laquelle doit être effectuée l'impression.

12. Tampon selon l'une quelconque des revendications 10 et 11, **caractérisé en ce que** ladite face recto a une surface structurée pour l'impression.

13. Procédé pour préparer un tampon pour lithographie douce, en particulier pour l'impression de microcontacts, comprenant les étapes consistant à :

(a) disposer d'un original ayant une surface et une structure en relief sur ladite surface,
(b) disposer d'une feuille polymère,
(c) presser ledit original dans ladite feuille polymère, qui laisse ainsi une empreinte de ladite structure en relief sur ladite feuille polymère,
(d) retirer ledit original de ladite feuille polymère portant l'empreinte, ladite feuille polymère étant faite en un polymère ionomère, de préférence un copoly(éthylène/acide méthacrylique).

14. Procédé selon la revendication 13, dans lequel l'étape c) est effectuée à une température élevée, située dans la plage allant de 80°C à 150°C, de préférence de 100°C à 135°C, mieux encore de 120°C à 130°C, tout spécialement d'environ 125°C.

15. Procédé selon la revendication 14, dans lequel ledit original ou ladite feuille polymère ou les deux sont maintenus à ladite température élevée durant l'étape c).

16. Procédé selon l'une quelconque des revendications 13 à 15, dans lequel ledit copoly(éthylène/acide méthacrylique) est un polymère dans lequel l'éthylène a été soumis à une copolymérisation statistique avec l'acide méthacrylique en un rapport de 10/1 à 100/1, de préférence > 10.

17. Procédé selon l'une quelconque des revendications 13 à 16, dans lequel ledit copoly(éthylène/acide méthacrylique) a une masse moléculaire moyenne située dans la plage allant de 50 000 à 200 000, de préférence de 100 000 à 150 000.

18. Procédé selon l'une quelconque des revendications 13 à 17, dans lequel, dans ledit copoly(éthylène/acide méthacrylique), tout ou partie des groupes carboxyle d'acide méthacrylique est sous la forme de carboxylate de zinc ou de carboxylate de sodium.

19. Procédé selon l'une quelconque des revendications 13 à 18, **caractérisé en ce que** ladite feuille est faite en un matériau capable d'atteindre un module de Young > 20 Mpa après chauffage.

20. Procédé selon l'une quelconque des revendications 13 à 19, dans lequel ladite feuille polymère portant l'empreinte a une face recto pour l'impression et une face verso opposée à ladite face recto, et, après l'étape d), un matériau siliconé durcissable est placé sur ladite face verso de ladite feuille polymère portant l'empreinte et ensuite durci, ladite feuille polymère portant l'empreinte étant ainsi au moins partiellement encastrée dans ledit matériau siliconé durci.

21. Procédé selon la revendication 20, dans lequel ladite face recto a une surface structurée pour l'impression.

22. Procédé selon l'une quelconque des revendications 20 et 21, dans lequel ledit matériau siliconé durcissable est un prépolymère de polydiméthylsiloxane, de préférence un prépolymère de vinyl-polydiméthylsiloxane, et est durci en présence d'un catalyseur, de préférence un catalyseur au platine, et de copolymères de méthylhydrosiloxane et de diméthylsiloxane.

23. Procédé selon l'une quelconque des revendications précédentes, dans lequel, après l'étape d), une surface, de préférence ladite face recto de ladite feuille polymère portant l'empreinte, est encore modifiée.

24. Procédé selon la revendication 23, dans lequel ladite surface est encore modifiée par un procédé choisi parmi un traitement au plasma, une modification chimique, et un traitement avec un tensioactif.

25. Tampon produit par le procédé de l'une quelconque des revendications 13 à 24.

26. Utilisation d'un tampon selon l'une quelconque des revendications 1 à 12 et 25 pour la lithographie douce, en particulier pour l'impression de microcontacts.

27. Utilisation selon la revendication 26, dans laquelle ledit tampon est encré par encrage par contact ou par encrage humide.

28. Utilisation selon l'une quelconque des revendications 26 et 27, pour l'impression de microcontacts de pistes ou fils conducteurs, en particulier de structures en grilles ou de structures en barres croisées, dans laquelle, de préférence, lesdites structures en grilles et/ou lesdites structures en barres croisées sont des structures faites en fils conducteurs, mieux encore ayant une largeur située dans la plage allant de 10 nm à 200 nm, et/ou dans laquelle, de préférence, lesdites structures en grilles et/ou lesdites structures en barres croisées comprennent des pastilles, mieux encore ayant une longueur de bord d'environ 100 μm.

29. Procédé d'impression de microcontacts, comprenant les étapes consistant à :

e) disposer d'un tampon selon l'une quelconque des revendications 1 à 12 et 25,
f) encrer ledit tampon, de préférence par encrage par contact ou encrage humide,
g) presser ledit tampon encré sur un substrat.

30. Utilisation d'un matériau polymère ionomère tel que défini dans l'une quelconque des revendications 1 à 6, dans un tampon pour lithographie douce, en particulier pour l'impression de microcontacts.

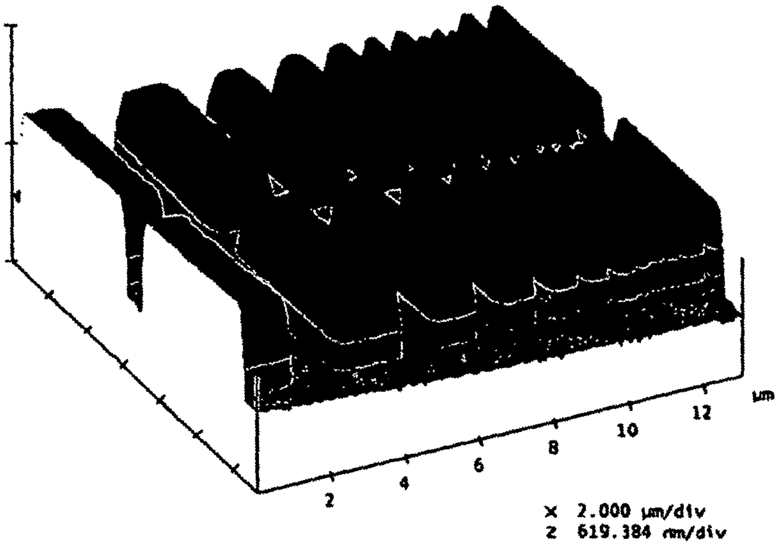

Fig. 1

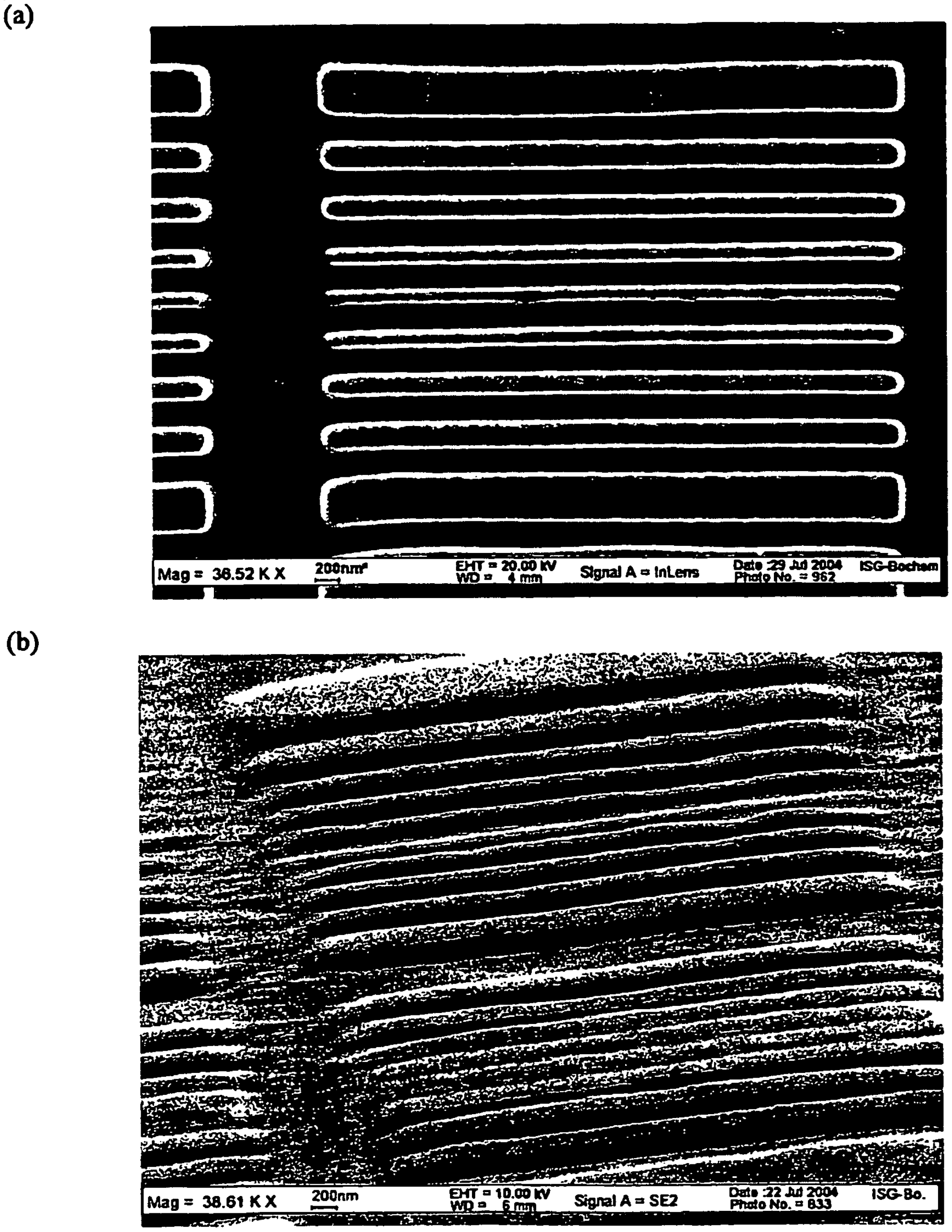

Fig. 2 a and b: SEM picture of a Surlyn^{TM} stamp surface with 75nm smallest bar width.

Fig. 2a and b

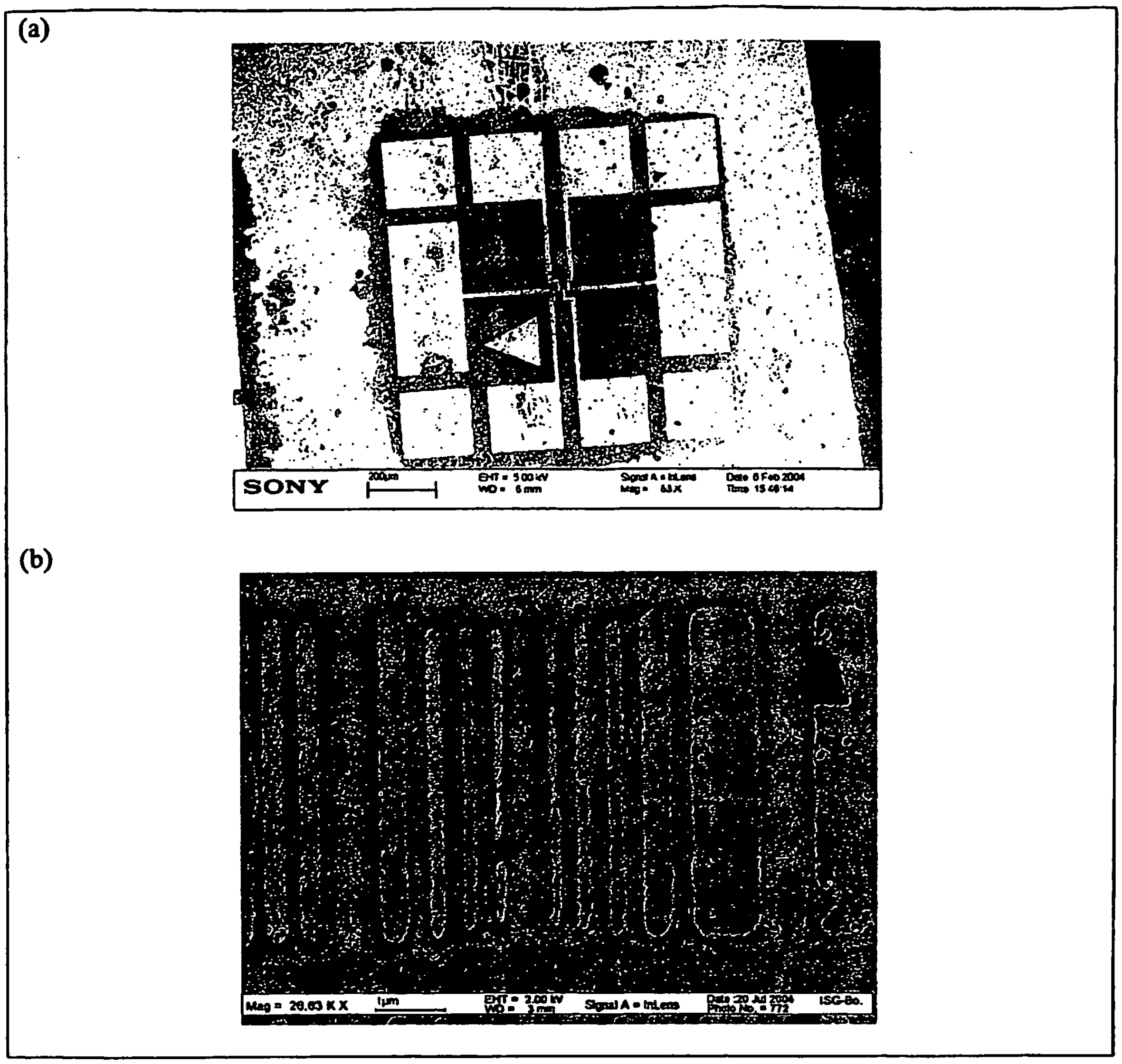
(a)
SONY
200µm
EHT = 5.00 kV
WD = 6 mm
Signal A = InLens
Mag = 63 X
Date 6 Feb 2004
Time 15:48:14
(b)
Mag = 26.63 K X
1µm
EHT = 2.00 kV
WD = 3 mm
Signal A = InLens
Date 20 Jul 2004
Photo No. = 772
ISG-Bo.

Fig. 3

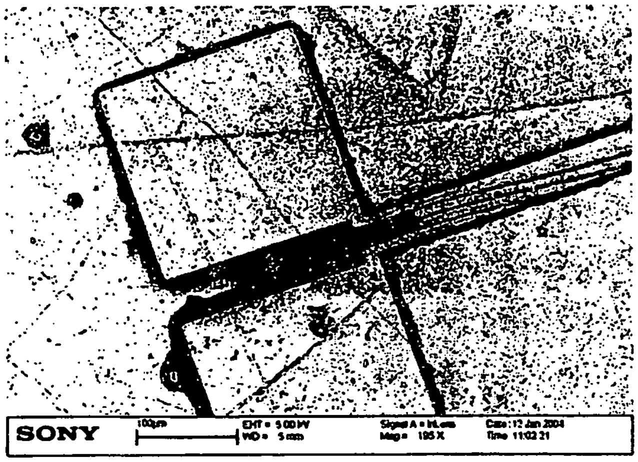
SONY
100µm
EHT = 5.00 kV
WD = 5 mm
Signal A = InLens
Mag = 195 X
Date :12 Jan 2004
Time 11:02:21

Fig. 4

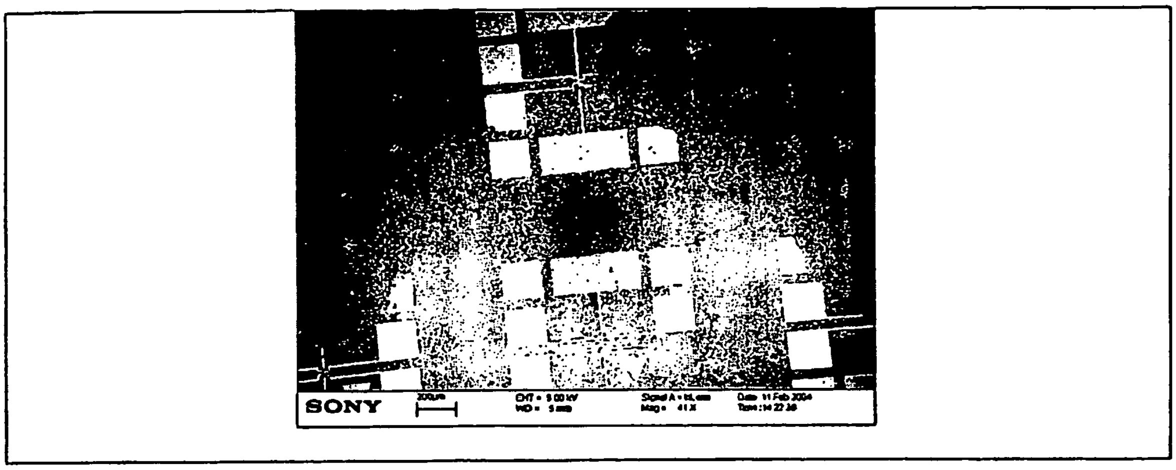
SONY
200µm
EHT = 5.00 kV
WD = 5 mm
Signal A = InLens
Mag = 41 X
Date: 11 Feb 2004
Time: 14:22:38

Fig. 5

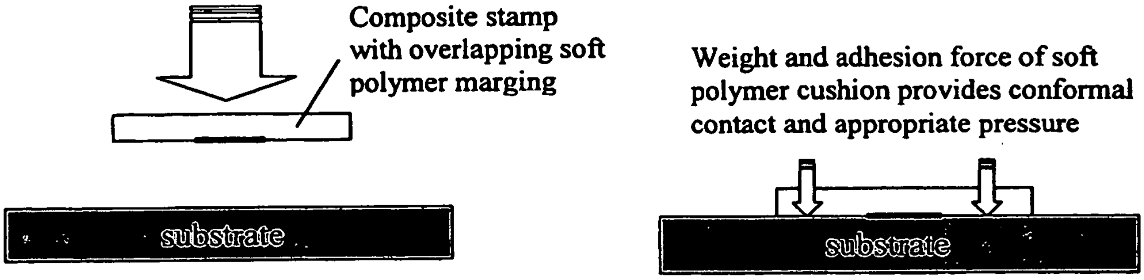
Composite stamp
with overlapping soft
polymer marging
substrate
Weight and adhesion force of soft
polymer cushion provides conformal
contact and appropriate pressure
substrate

Fig. 6

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