Surface Polymers for Improved Adhesion to Substrates of Deposited Polymer Films

Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Application No. US 63/571,721 titled "Surface Polymer for Improved Polymer Adhesion to Substrates" filed March 29, 2024, which is incorporated by reference in its entirety herein.

Field

The disclosure relates to the adhesion of polymer films to substrates decorated with surface polymers, and methods for forming the same.

Background

A bonding material - an adhesive - may be used to adhere two types of materials. However, depending on the intended application, options for a suitable adhesive for adhering the materials may be very limited as the presence of the adhesive may interfere with the intended function of the individual materials; furthermore, the bonding strength of these adhesives may not be sufficient for the stresses exerted on the bonded materials; yet furthermore, adhesives may not be compatible with the method for depositing the second material on the first material – for example, deposition from solution of a polymer on to a solid substrate.

Thus, there is a need for improving adhesion between different materials and methods for achieving the same.

Summary

In an aspect, the present disclosure relates to a method of adhering a polymer to a surface of a substrate comprising providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate, exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate, and depositing a polymer on the at least one surface of the substrate, to provide an adhering interface between the surface polymer and the polymer. The deposited polymer may be a thin film of polymer material. The polymer may be solubilized in a solvent. The surface polymer may comprise one or more functional groups compatible with one or more functional groups in the polymer. The one or more functional groups of surface polymer

may be selected from hydroxyl groups, amine groups, and amide groups. The one or more functional groups of the polymer may be methyl ester groups. The method may be such, wherein the monomer is comprised in a reaction composition comprising a catalyst, a ligand, an activator, and a solvent. The catalyst may be obtained from copper (Cu), iron (Fe) or ruthenium (Ru). The ligand may be selected from *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridyl-methyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethyl-ethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), and/or 2,2'-bipyridyl (BiPy). The activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose, glucose with glycose oxidizing enzyme (GO_x), and/or pyrogallic acid. The solvent may be an aqueous solvent. The reaction composition may further comprise a buffer. The reaction composition may further comprise a halogen salt. The reaction composition may further comprise a surfactant. The reaction composition may further comprise a polyquaternium compound. The surface polymer may comprise the surface polymer comprises poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), or poly(glycidyl methacrylate) (PGMA), and the polymer is poly(methyl methacrylate) (PMMA), or poly(amic acid). The polymer may be poly(acrylic acid) (PAA), poly(amic acid), or poly(methyl methacrylate) (PMMA). The surface polymer may be poly(methyl methacrylate) (PMMA), and the polymer may be poly(methyl methacrylate) (PMMA). Following depositing of the polymer, the substrate, and, thus, the interface between the surface and the polymer may be dried, UV cured, or post-baked. The substrate may comprise silicon, copper, glass, ceramic and/or steel. The polymer may be deposited, for example, by doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

In an aspect of the present disclosure, a device stack is provided, the device stack comprising a substrate with a first surface, a surface polymer on at least a portion of a first surface covalently attached to the substrate via polymerization initiators covalently attached to the substrate, and a deposited polymer covering and adhering to at least a portion of the surface polymer. The deposited polymer may form a thin film on the substrate. The thin film may have a thickness in the range 1 nm to 30 μm. The substrate of the device stack may comprise silicon, copper, glass, ceramic and/or steel. The polymer may be deposited by, for example, doctor blading, spin coating,

spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating. The surface polymer of the device stack may comprise the surface polymer comprises poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), or poly(glycidyl methacrylate) (PGMA), and the polymer is poly(methyl methacrylate) (PMMA), or poly(amic acid). The polymer of the device stack may be poly(acrylic acid) (PAA), poly(amic acid), or poly(methyl methacrylate) (PMMA). The surface polymer may be poly(methyl methacrylate) (PMMA), and the polymer may be poly(methyl methacrylate) (PMMA).

In an aspect of the present disclosure, a device stack is provided, the device stack comprising a substrate with a first surface, a surface polymer on at least a portion of a first surface covalently attached to the substrate via polymerization initiators covalently attached to the substrate, and a deposited polymer covering and adhering to at least a portion of the surface polymer, wherein the surface polymer may be formed by providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate, and exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate. The reaction composition may further comprise a catalyst, a ligand, an activator, and a solvent. The catalyst may comprise copper (Cu), iron (Fe) or ruthenium (Ru). The ligand may be selected from *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), and/or 2,2'-bipyridyl (BiPy). The activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose, and/or pyrogallic acid. The solvent may be an aqueous solvent. The reaction composition may further comprise a buffer. The reaction composition may further comprise a halogen salt. The reaction composition may further comprise a surfactant. The reaction composition may further comprise a polyquaternium compound. The polymer may be deposited by, for example, doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

In an aspect of the present disclosure, a method of preparing a device stack as described herein is provided, the method comprising providing the substrate, wherein surface polymers are present on

at least a portion of the surface of the substrate, providing a polymer, and depositing the polymer on the surface of the substrate to provide an adhering interface between the surface polymer and the polymer. The deposited polymer may be a thin film of polymer material. The polymer may be provided solubilized in a solvent. The polymer may be deposited by, for example, doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating. Following the depositing, the device stack comprising the substrate, the surface polymer and the polymer, may be dried, UV cured and/or post-baked. The substrate may comprise silicon, copper, glass, ceramic and/or steel, for example.

In an aspect of the present disclosure, a system for forming a device stack as described herein is provided, the system comprising a reaction composition container containing a reaction composition, said reaction composition comprising a monomer, a catalyst, a ligand, a catalyst activator, and a solvent, a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time, wherein the controlled time may be sufficient for surface polymers to be formed on the portion of the polymerization initiator-modified substrate, a polymer deposition system for depositing a polymer at least over a portion of the formed surface polymer, wherein the substrate displacement device may further be configured for bringing the surface polymer coated substrate into the polymer deposition system for a controlled time, and wherein the controlled time may be sufficient for depositing a polymer on at least a portion of the surface polymers, and optionally a device for drying, curing, or post-baking the polymer following the depositing of the polymer. The substrate displacement device may comprise any one of a conveyor system, a programmable mechanical arm, or a roll-to-roll mechanism. The system may further comprise a polymerization initiator container containing a polymerization initiator agent, wherein the substrate displacement device may further be configured to bring the portion of the substrate for attachment of polymerization initiators into contact with the polymerization initiator agent to form polymerization initiators at the substrate surface, prior to bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition. The system may further comprise a cleaning container, the cleaning container containing a cleaning agent, wherein the substrate displacement device may be configured to bring the portion of the polymerization initiator-modified substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition, and optionally the substrate displacement device may be configured

to bring the portion of substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator. The polymerization initiator container may be a vacuum oven. The polymer deposition system may comprise a doctor blade coater configured to spread the polymer on to the surface polymer, a spin coater configured to spin coat the polymer on to the surface polymer, a comma coater configured to spread the polymer on to the surface polymer, a slot-die coater configured to spread the polymer on to the surface polymer, a spray coater for spraying the polymer in a volatile carrier solvent on to the surface polymer, a dip coating tank for applying the polymer on to the surface polymer, a flow coating tool for gravity flowing the polymer in a volatile carrier solvent over the surface polymer, or a vacuum chamber configured for physical vapor deposition of the polymer on to the surface polymer.

Description of the Drawings

Certain embodiments of the present disclosure are illustrated in the accompanying drawings. The drawings are, however, in no way intended to limit the present disclosure. In the drawings:

Fig. 1 is a schematical representation of a substrate 130 decorated with surface polymers 140, wherein a polymer 170 is adhered to the substrate 130 through surface polymers 140.

Fig. 2 is a schematical representation of doctor blading a polymer onto a substrate decorated with surface polymers.

Fig. 3 schematically shows the doctor blading of a polymer on a substrate.

Fig. 4 schematically shows the crosshatch test: the first illustration shows the substrate decorated with surface polymers 200 with the doctor bladed polymer 210; the second illustration show the crosshatches 220 after cutting; the third illustration shows the substrate after applying the tape 230; the fourth illustration shows crosshatches 240 remaining on the substrate after peeling off the tape 230 and the peeled-off crosshatches 250, 260 after peeling off the tape 230. See also Example 5.

Fig. 5 shows PAA deposited by doctor blading on unfunctionalized (blank) Si substrates, see Example 12.

Fig. 6 shows the substrates of Fig. 5 after cutting the crosshatches, see Example 12.

Fig. 7 is a microscopic view (Dino-Lite Universal microscopic photograph) of the substrates of Fig. 6 after applying and peeling off the tape, see Example 12.

Fig. 8 shows PAA deposited by doctor blading into Si substrates with PMAA surface polymers, see Example 12.

Fig. 9 shows the PMAA substrates of Fig. 8 after cutting the crosshatches, see Example 12.

Fig. 10 shows the PMAA substrates of Fig. 9 after applying and peeling off the tape (Dino-Lite Universal microscopic photographs of the PMAA substrates), see Example 12.

Fig. 11 shows the blank stainless steel substrates after doctor blading with PAA polymer, see Example 12.

Fig. 12 shows the substrates of Fig. 11 after crosshatch cutting, see Example 12.

Fig. 13 shows the substrates of Fig. 12 after applying and peeling off the tape, see Example 12.

Fig. 14 shows Dino-Lite Universal microscopic photographs of the substrates shown in Fig. 13, see Example 12.

Fig. 15 shows PMAA surface polymer-functionalized stainless steel substrates after doctor blading with PAA polymer, see Example 12.

Fig. 16 shows the substrates of Fig. 15 after crosshatch cuttings, see Example 12.

Fig. 17 shows the substrates of Fig. 16 after applying the tape and peeling off the tape, see Example 12.

Fig. 18 shows Dino-Lite Universal microscopic photographs of the substrates of Fig. 17, see Example 12.

Fig. 19 schematically shows battery components, including positive electrode current collector, negative electrode current collector, and separator decorated with surface polymer.

Fig. 20 shows the crosshatch tests of Example 13 in respect of blank substrate, CPTMS-modified substrates, and substrates modified with a range of surface polymers, and doctor bladed with PMMA polymer.

Fig. 21 shows the crosshatch tests of Example 14 in respect of blank substrate, CPTMS-modified substrate, and substrates modified with a range of surface polymers, and doctor bladed with PI polymer.

Fig. 22 shows the crosshatch tests of Example 15. A) shows the substrate with PMMA surface polymers and doctor bladed PMMA polymer. B) shows the blank substrate doctor bladed with PMMA polymer.

Fig. 23 shows zoomed sections of the substrates shown in Fig. 22 A) and B).

Fig. 24 shows the ISO and ASTM crosshatch scoring.

Fig. 25 is a schematic illustration of a system for forming surface polymers on at least a portion of a substrate.

Fig. 26 is a schematic illustration of an exemplary substrate displacement device, the substrate displacement device comprising a roll-to-roll processing device, in accordance with an embodiment.

Detailed Description

The present disclosure relates to the adhesion of polymers to a substrate. The polymer may be adhered to at least a portion of at least one surface of the substrate, where the at least a portion of at least one surface of the substrate is decorated with a surface polymer, formed by propagating the surface polymers from polymerization initiators on the at least a portion of at least one substrate surface. For adhering of the polymer, the polymer may be deposited on the substrate decorated with surface polymer, so as to create an interface between the surface polymer and the polymer. The substrate may subsequently be subjected to a post-treatment to promote the adhesion. Post-treatment includes, but is not limited to, drying, UV-curing, and post-baking.

In an aspect, the present disclosure relates to a method of adhering a polymer to a surface of a substrate comprising providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate, exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate, and depositing a polymer on the at least one surface of the substrate, to provide an adhering interface between the surface polymer and the polymer.

The deposited polymer may be a thin film of polymer material. The term "thin film" is intended to include a polymer film which has a sufficient thickness to suit the intended application. The thin film may generally have a thickness in the range from less than 1 nm up to several microns. When the intended application includes electronics, the thin film may have a thickness of up to several microns. When the intended application includes Extreme Ultraviolet lithography (EUV), the thin film may have a thickness in the range of less than 1 nm and up to approximately 10 nm. When the intended application is semiconductor applications, the thin film may have a thickness in the range of less than 1 nm and up to approximately several microns. However, when the intended application is formation of anode layers in electrochemical cells, e.g., thin film batteries, the film may go beyond what is usually understood to be "thin films" and may have a thickness of up to 30 μm. The thin film thickness may be determined using methods usually applied within the relevant field of application.

The polymer may be deposited on the substrate decorated with surface polymers applying various procedures. Such procedures include, but are not limited to doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating. For depositing of the polymer, the polymer may be solubilized in a suited solvent. The solvent may be chosen so as to provide good solubility or dispersibility of the polymer to make the depositing as easy and evenly as possible. The solvent of choice may, i.a., depend on the polarity, the molecular weight, the branching, the crosslinking degree, the crystallinity, and the hydrogen bonding tendency of the polymer.

For forming efficient adhering of the interface between the surface polymer and the polymer, the surface polymer and the polymer may comprise functional groups mutually compatible. Thus, the surface polymer may comprise one or more functional groups compatible with one or more functional groups in the polymer. The one or more functional groups of the surface polymer may be selected from hydroxyl groups, amine groups, amide groups, methyl esters, allyl functionalities, and oxirane rings. The one or more functional groups of the polymer may be methyl ester groups, imides, or carboxylic acids. E.g., the surface polymer may comprise functional groups that are hydrogen bonding donors. Non-limiting examples include poly(methacrylic acid) (PMAA), poly(2-hydroxyethyl methacrylate) (PHEA), poly(acryl amide) (PAA), and poly(2-hydroxyethyl acrylate) (PHEA). E.g., the surface polymer contains functional groups that are not hydrogen bonding donors. Non-limiting examples include poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), and poly(glycidyl methacrylate) (PGMA).

Thus, the polymer may comprise one or more functional groups compatible with one or more functional groups in the surface polymer.

In accordance with an aspect of the present disclosure, there is provided a substrate decorated with surface polymers on at least a portion of at least one surface of the substrate and further having a layer of a polymer on the surface of the substrate, wherein the polymer is adhered to the surface of the substrate through the surface polymers. Fig. 1 is a schematical representation of a substrate 130 decorated with surface polymers 140, wherein a polymer 170 is adhered to the substrate 130 through the surface polymers 140.

In accordance with the present disclosure, the reaction composition for forming surface polymers from polymerization initiators on the substrate may in addition to the monomer comprise a catalyst, a ligand, an activator, and a solvent. The components of the reaction composition, that is the monomer, the catalyst, the ligand, the activator, and the solvent, may be combined in any order. E.g., the catalyst and the ligand may be provided in a solvent and may be mixed with the activator dissolved in a solvent prior to the addition of the monomer. E.g., the monomer, the catalyst and the ligand may be provided in a solvent and may be mixed with the activator dissolved in a solvent. E.g., the catalyst, the ligand, the catalyst may be dissolved in the monomer (acting as solvent), if the monomer is in liquid form.

Some methods for preparing a substrate for surface polymer formation, i.e. attaching polymerization initiators, have been described in the art. A brief description of processes that may be used in connection with the present disclosure is given below. However, it is to be understood that alternative processes may also be suited and workable within the context of the present disclosure.

Attachment of polymerization initiators to a surface of a substrate may as mentioned be performed by various procedures. Polymerization initiators are covalently bonded to the surface of the material, see, e.g., WO 2014/0075695. The polymerization initiators may be provided with a predefined surface chemistry to enable attachment onto the surface of the substrate, depending on the nature of the substrate. Non-limiting examples of suitable chemistries for attaching polymerization initiators on surfaces include but are not limited to aryl diazonium salts, organosilanes, organothiols, organophosphonic acids, organophosphonates, catechols, iodonium salts, alkenes, alkynes, and sol-gel coatings. Surface anchored polymerization initiators can be prepared as multilayer films or monolayer films. Monolayer films can be densely packed (full monolayer coverage) or partly packed, covering all or only a part of the available surface. The density of the polymerization initiator influences the density of the subsequently formed surface polymer. Density of initiators would be understood by persons of ordinary skill as the number of polymerization initiators per unit area of the substrate.

The attachment of polymerization initiators usually follows a 1-step or a 2-step process. The 1-step process applies grafting of benzyl halide (like benzyl chloride) or secondary or tertiary halide moieties onto the surface of the substrate either by diazonium or silane grafting. The benzyl halide

and secondary and tertiary halide moiety act as the polymerization initiator for the following surface-initiated polymerization. The 2-step process usually applies surface grafting of an initial organic compound with a nucleophilic group, and in a second step using the nucleophilic group to attach an initiator moiety. The nucleophilic group may include a hydroxyl or amine group. Then, the nucleophilic group may be reacted with an electrophile to add an initiator moiety, forming a covalent bond between the two. The initiator moiety may be, e.g., benzyl halide and tertiary halide moieties.

The polymerization initiator attachment process is further described below. The procedures may in general apply to all types of substrates.

Silane grafting 1-step:

Initiators can be attached to a surface in one step by silane grafting of trialkoxysilane with benzyl halide or tertiary halide groups. The silane grafting is normally done either by vapor deposition, in solution, by spray coating, or paint-on coating.

Diazonium grafting 1-step:

Initiators can be attached to a surface in one step by grafting aryl diazonium salts with benzyl halide groups. The diazonium grafting is normally done either by activating the aryl diazonium salt electrochemically or chemically or by letting it react spontaneously. Diazonium salts can be pre-synthesized before being used for grafting reaction or formed in-situ during grafting reaction from a set of precursors added to the grafting reaction solution.

Diazonium grafting 2-step:

Another route of initiator attachment is by a two-step process. The first step being grafting of an aryl diazonium salt that contains a nucleophilic group (alcohol or amine). In a second step a nucleophilic acyl substitution reaction adds a halogen containing group, giving the attached polymerization initiator.

Silane grafting 2-step:

The first step being grafting of a silane that contains a nucleophilic group (alcohol or amine). In a second step, a nucleophilic acyl substitution reaction adds a halogen containing group, giving the attached polymerization initiator.

Other processes for attaching first polymerization initiators may be applied. E.g., the polymerization initiator CPTMS (*p*-chloromethyl)phenylethyl]trimethoxysilane) may be attached using a vapor deposition method or a dipping method. E.g., the polymerization initiator BiBB (bromoisobutyl bromide) may be attached by a dipping method. A polymerization initiator may also be formed by incorporation or attachment of a chloromethyl moiety, a sulfonyl chloride moiety, or benzylchloride moiety.

If only specific areas of a material surface are to be coated with first polymerization initiators, the area(s) with functional polymerization sites may be blocked, e.g., chemically or by using a foil, a seal or a cover, or etched, or masked, protected, or defined by lithographic patterning.

The surface polymer formed on a surface of a substrate may be composed of several types of monomeric units.

Suitable examples of monomers for surface polymerization and polymer deposition are indicated below.

Thus, non-limiting examples of appropriate monomer types include anionic, cationic, zwitterionic, protic and aprotic monomers, and include acrylates, methacrylates, halogen-substituted alkenes, acrylamides, methacrylamides, and styrenes, as well as mixtures thereof. The generic monomer structure comprises a polymerizable part (a vinyl group), which in certain embodiments is connected to a functional group responsible for the specific functionality (e.g., adhesion, permeability, electric and ionic conductivities) of the certain monomer through a certain linker chemistry.

For acrylate monomers, non-limiting examples of functional moieties include but are not limited to alkyl groups, aryl groups, sulfonates, fluorosulfonates, carboxyls, metal carboxylates, ethers, poly(ether) groups, bis(sulfonyl)amides, fluorinated sulfonates, perfluoroalkyl carboxylate,

borate, fluorinated borate, borate ester derivatives, bis(trifluoromethane)sulfonimide, triflimides and derivatives thereof, halogenated alkyl chains, and mono-, di-, and tri-alkoxy silanes.

The polymerizable part and the functional part of monomer can, in certain embodiments, be connected by a linker moiety. Non-limiting examples of appropriate linker chemistries include but are not limited to alkyl chain, esters, ethers, poly(ethers), amines, amides, aryls, and any combination(s) thereof. Non-limiting examples of appropriate acrylate monomers containing alkyl linkers include but are not limited to methyl acrylate, ethyl acrylate, and lauryl acrylate. Non-limiting examples of monomers using ether and poly(ether) linker chemistry include but are not limited to poly(ethylene glycol) methyl ether acrylate, and poly(ethylene glycol) acrylate. Non-limiting examples of monomers without linker chemistry include but are not limited to acrylic acid, lithium acrylate, sodium acrylate, and vinyl imidazole.

For methacrylate monomers, non-limiting examples of appropriate functional moieties include but are not limited to carboxylic acids, metal carboxylates, esters, alkyl alcohols, oxiranes (epoxides), linear and branched alkyl groups, alkenes, aryl groups, sulfonates, fluorosulfonates, bis(sulfonyl)amides, fluorinated sulfonates, perfluoroalkyl carboxylate, borate, fluorinated borate, borate ester derivatives, bis(trifluoromethane)sulfonimide, triflimides, and derivatives thereof, halogenated alkyl chains, and mono, di, and tri-alkoxy silanes.

Non-limiting examples of linker chemistries include but are not limited to alkyl chains, esters, ethers, poly(ethers, amines, amides, aryls, and any combination(s) thereof.

Non-limiting examples of methacrylate monomers include but are not limited to methacrylic acid, lithium methacrylate, sodium methacrylate, methyl methacrylate (MMA, potassium 3-sulfpropyl methacrylate (K-SPMA, 2-hydroxyethylmethacrylate (HEMA, glycidyl methacrylate (GMA, ethyl methacrylate, *n*-butyl methacrylate (BuMA, *tert*-butyl methacrylate (tBMA, lauryl methacrylate, (((perfluorobutyl)sulfonyl)oxy)methyl methacrylate, 3-(N-((trifluoromethyl)sulfonyl)sulfamoyl)propyl methacrylate, 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl methacrylate (HFDMA, allyl methacrylate, 2-((triethoxysilyl)oxy)ethyl methacrylate, and 2-(3-(triethoxysilyl)propyl)ethyl methacrylate.

Non-limiting examples of acrylate monomers include but are not limited to methyl acrylate (MA), tert-butyl acrylate (tBA), lauryl acrylate (LA), and 2-hydroxyethylacrylate (HEA).

Non-limiting examples of appropriate halogen-substituted alkene monomers include but are not limited to vinyl chloride, vinylidene difluoride, tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene.

Non-limiting examples of appropriate acrylamide monomers include but are not limited to acrylamide, *N-iso*-propylacrylamide, *N-tert*-butylacrylamide, and *N*-hydroxyethyl acrylamide.

Non-limiting examples of appropriate methacrylamide monomers include but are not limited to *N-iso*-propylmethacrylamide, methacrylamide, *N-tert*-butylmethacrylamide, and *N*-hydroxyethyl methacrylamide.

Non-limiting examples of appropriate styrene monomers include but are not limited to styrene, 4-methylstyrene, 2,3,4,5,6-pentafluorostyrene, *p*-divinylbenzene, 4-chlorostyrene, sodium 4-vinylbenzenesulfonate, lithium 4-vinylbenzenesulfonate, and 4-vinylphenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate.

Monomer(s) may be chosen to provide compatibility/adhesion/elasticity, as appropriate for a specific application. Monomer(s) can also be selected to enhance or diminish electrical and/or ionic conductivity, and/or permeability. Monomers may be chosen to improve interface stability of a surface in question. Monomers may suitably be used in an amount corresponding to a percentage of the total volume of the reaction medium. For example, a liquid monomer may constitute, e.g., 0.5 vol%, 2 vol%, or 10 vol% of a reaction composition. For example, a solid monomer may constitute, e.g., 0.5 wt%, 2 wt%, or 10 wt% of the reaction composition. In each application, an amount of monomer may be chosen to provide a desired polymer formation kinetics, solubility of the monomer, and cost of the monomer.

In each application, the amount of monomer may be chosen to obtain desired polymerization kinetics and polymerization rate, solubility of the monomer, and cost of the monomer. The preferred range for the amount of monomer is in most cases 0.5 vol% to 50 vol%.

Following formation of the polymer molecule, the formed surface polymer is indicated with a "P" as prefix to the monomer. By way of example, methyl methacrylate monomer is denoted MMA, and after polymerization, the polymer molecule is denoted PMMA. Likewise, 2-hydroxyethyl methacrylate is denoted HEMA, and after polymerization, the polymer molecule is denoted PHEMA.

Surface polymers comprising copolymers are also within the scope of the present disclosure.

Within the present context, the expression "copolymer" or "copolymers" is intended to mean a surface polymer as defined herein comprising at least two different monomeric repeat units. Copolymers may be formed by copolymerizing different types of monomers or by subsequent partial chemical modification of a homopolymer (within the surface polymer) to add a chemical modification of one type of monomeric repeat unit to obtain a different type of monomeric repeat unit. Hence, two or more functional groups (e.g., halogen atoms, hydroxyl groups, or amine groups) can be incorporated, resulting in surface polymers with a unique set of combined properties, each of which is inherent from individual monomers. Thus, copolymerization is a powerful tool to modulate surface polymer properties by combining the properties of two or more monomers. The resulting copolymer may exhibit properties that cannot be achieved by polymerization of a single monomer. A handle for modulating the properties may be by varying the incorporation of the co-monomers, e.g. by varying the initial ratios of the co-monomers. Copolymerization may proceed from viable ends on the already formed surface polymer.

When more than one type of monomer is polymerized simultaneously, the polymerization can result in statistical, alternating, and in some special cases block copolymers depending on the relative reactivity ratio of the monomers. The reactivity ratio of a monomer in copolymerization is defined by the ratio of the rate at which a monomer adds to a growing chain of its own type versus the rate at which it adds to a growing chain comprised of the other monomer. For statistical copolymers, the distribution of the different types of monomeric repeat units may follow different statistical laws such as Bernoullian (zero-order Markov), first- or second-order Markov depending on the polymerization method and the reactant composition. "*Random copolymer*" is the most common terminology used to describe *statistical copolymers* irrespective of the type of distribution.

The structures of statistical/random copolymers and alternating copolymers can be symbolized as follows (---ABAABABBAABAAABBBA---) (---ABABABABABAB---), wherein A and B represent two different type of monomeric repeat units. The structure of block copolymers is represented by two or more homopolymer blocks of different monomeric repeat units, connected by covalent linkages, and may be represented by A_mB_n (AB diblock), $A_mB_nA_m$ (ABA triblock), $(A_mB_n)_p$ (AB multiblock), $A_mB_nC_p$ (ABC triblock) and so on. While statistical/random copolymers that are, in general, prepared by simultaneous copolymerization of more than one monomer, block copolymers are, in general, prepared by sequential polymerization of different types of monomers. Thus, a considerable structural variability is possible for *block copolymers* due to the additional variability such as the number of blocks and the block lengths (m, n etc.). Alternating, statistical and random copolymers are designated as poly(A-alt-B), poly(A-stat-B), poly(A-ran-B)/poly(A-r-B), wherein A and B represent two different types of repeat units. In the present disclosure, the recent literature trends and therefore any polymer that has been prepared by simultaneous copolymerization of more than one monomer will be called as random copolymer, symbolized as poly(A-ran-B). Block copolymers are designated as poly(polyA-block-polyB)/poly(polyA-b-polyB). As mentioned above, these different types of copolymers may be denoted "co", e.g. poly(polyA-co-polyB) in the absence of a more specific differentiation. In the above, a prefix "P" may replace the term "poly".

The copolymers may be block-copolymers, random copolymers, or binary mixed polymers, where two or more separate monomers are used to propagate the surface polymer for different surface polymer architectures. Herein, the term "copolymer" is intended to include block copolymers, random copolymers, and binary mixed polymers (e.g., "PHEMA-co-PHEA" being a copolymer of PHEMA and PHEA). Sometimes, "r" may be used to denote random copolymers (e.g., "PHEMA-r-PHEA" being a random copolymer of PHEMA and PHEA). Sometimes "b" may be used to denote a block of one polymer and a block of another polymer (e.g., "PHEMA-b-PHEA" being a first block polymer of PHEMA, and a second block of PHEA).

It is expected that a wide range of different substrates will be useful in connection with the disclosure herein, however, suitable substrates should provide a surface, allowing firstly attachment of first polymerization initiators, and secondly formation of surface polymers of first polymer molecules from said first polymerization initiator sites. Suitable substrates include, but are not limited to, metal (like aluminum, steel, nickel, gold, silver, platinum, chrome, copper, iron

and alloys), glass, carbon, graphite, graphene, carbon black, monoclays, ceramics, composite materials, plastics, semiconductors, compound semiconductors (e.g., GeAs and InP), and particles (e.g., Si, metal, metal alloys and coated particles). The substrate may have any size, shape and structure, including an elongated structure, and may be in the form of pieces, threads, fibers, cables, wires, particles, nanoparticles, monolayers etc. Particles and nanoparticles may be uncoated or coated with another material and may further be in the form of aggregates (multiple (nano)particles forming an assembly of individual (nano)particles). Aggregates may in some cases be viewed as one (nano)particle.

Several procedures are available for forming surface polymers on at least a portion of a surface of a substrate. Among the procedures for formation of surface polymers, (ARGET) ATRP and SET-LRP are widely used. For the polymerizing chains to propagate, a monomer, a catalyst, a ligand and a solvent are needed. In (ARGET) ATRP and SET-LRP polymerizations, some reactions activate the catalyst, thereby, promoting polymerization, and at the same time, other reactions deactivate the catalyst to impede polymerization, and a suitable equilibrium between activating and deactivating catalyst-ligand species is set to control surface polymer propagation. SARA-ATRP and SET-LRP are described, e.g., in https://www.cmu.edu/maty/atrp-how/procedures-for-initiation-of-ATRP/SARA-ATRP-or-SET-LRP.html. Both the SET-LRP and (ARGET) ATRP method $CuCl_2$ or $CuBr_2$ in the case of ARGET ATRP, and Cu(0) in the case of SET-LRP. The Cu-catalyzed ARGET ATRP involves a halogen transfer between a dormant halogen capped species, P_n-X and Cu(I)X/L catalyst, resulting in the formation of a propagating radical (P_n radical) and $Cu(II)X_2$. The propagating radical undergoes polymerization with monomers, forming the growing polymer chain. Controlling the ratio between Cu(I)X/L and $Cu(II)X_2$/L allows in general more control of the polymer propagation.

Surface-Initiated Surface Polymer formation is described in WO 2024 155981 and WO 2019 196999. WO 2019 196999 describes the use of a catalyst based on, e.g., a Cu oxide, the Cu forming a dormant complex with the ligand (Cu(II)/L) which may be activated on demand to Cu(I)/L by an oxygen scavenger as catalyst activator, such as sodium ascorbate. The dormant catalytic system described in WO 2019 196999 is halogen free at least to the extent that no halogen source is used to prepare the catalyst/ligand complex in contrast to SET-LRP and ARGET ATRP (use of Cu chlorides or Cu bromides).

Catalysts to be used herein for forming surface polymers may be selected from copper (Cu), iron (Fe), tin (Sn), aluminum (Al), cadmium (Cd), tungsten (W), rhenium (Re), ruthenium (Ru), platinum (Pt), titanium (Ti), manganese (Mn), nickel (Ni), samarium (Sm), or palladium (Pd). In particular, the catalyst may be obtained from Cu, Fe or Ru. Specific examples of such catalysts include Cu_2O, CuO, CuCl, $CuCl_2$, CuBr, $CuBr_2$, $FeCl_3$, $FeBr_3$, $Fe_2(SO_4)_3$, $FeCl_2$, $FeBr_2$, $FeSO_4$, $RuCl_3$ and $RuCl_3$ hydrate as well as combinations thereof. The catalyst concentration in the reaction composition is typically in the range 0.001–1 mM. The concentration of catalyst in the reaction composition is preferrable in the range 0.02–0.32 mM, for example 0.02 mM, 0.04 mM, 0.08 mM, 0.16 mM, or 0.32 mM. The activator for the catalyst (e.g., an oxygen scavenger) may be used in excess compared to the catalyst. Excess catalyst activator may, e.g., be 10-500 times. The catalyst activator is responsible for the turnover between oxidized deactivating and/or activating catalyst states. It is presently believed that the principal reaction pathway for catalyst activation is reduction, that is, the catalyst activator is a species which is capable of reducing the catalyst of the complex between the catalyst and the ligand from its inactive state to its catalytically active state, where surface polymer formation can take place. Examples of suited catalyst activators are sodium ascorbate, ascorbic acid, hydrazine, hydrazine hydrate, sodium hypophosphite, glucose, glucose with oxidizing enzyme (GO_X), tin 2-ethylhexanoate, sodium phenoxide, sodium dithionite, and a mixture of iron powder and sodium chloride.

Ligands to be used herein include, but are not limited to, nitrogen-containing ligands. Non-limiting examples of such nitrogen-containing compounds are bi-, tri-, or tetradentate amine ligands (containing two, three or four amine substituents) which are aliphatic and/or aromatic in nature. In particular, such ligands include *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine), TMEDA (tetramethylethylenediamine), Me_4Cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraaza-cyclotetradecane), and 2,2'-bipyridyl (BiPy), and combinations thereof. The amount of ligand in the reaction composition is defined as a ratio to the concentration of catalyst in the reaction composition. The ratio of ligand to catalyst in the reaction composition is in the range 0.001:1 – 1000:1. The ratio of ligand to catalyst in the reaction composition is preferrable in the range 0.005:1 – 100:1, for example 0.13:1, 0.5:1, 1.0:1, 2.0:1, 3.5:1, 7.5:1 or 12:1. In general, excess amount ligand as compared to amount catalyst is preferred.

The catalyst and the ligand form a complex. One, two, three or even four ligands may form complexes with one catalyst.

The reaction composition may comprise a solvent. Suitable solvents include but are not limited to alcohols, dipolar aprotic solvents (for examples, tetrahydrofuran, methyl acetate, ethyl acetate, butyl acetate, dimethyl sulfoxide, dimethyl formamide), methylene carbonate, ethylene carbonate, propylene carbonate, ethyl lactate alcohol, toluene, ionic liquids, supercritical CO_2, and water, as well as mixtures thereof. E.g., the solvent may be a mixture of one or more miscible solvents. E.g., the solvent may be an aqueous solvent, such as a mixture of water and one or more alcohols. Alcohols include, but are not limited to, methanol, ethanol, and isopropanol.

The reaction composition may further comprise a buffer. Buffers usually are aqueous. Suitable buffers include carbonate buffers, glycine buffers, citrate buffers, phosphate buffers, acetate buffers, ammonium buffers (ammonium chloride/ammonia), formate buffers, sodium ascorbate/ascorbic acid buffers, and/or zwitterionic buffers such as Good's buffers. Good's buffer include MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The buffer may provide stabilization of the reaction composition during the surface polymer formation.

The reaction composition may further comprise an additive in the form of a surfactant and/or a polyquaternium compound. Suitable surfactants include sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride. Suitable polyquaternium compounds include polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

The reaction composition may further comprise a halide compound for increasing the "livingness" of the surface polymerization of monomers. A "living" polymerization refers to a polymerization where the rate of termination is minor in comparison to the rate of propagation of polymer molecules from the polymerization initiators. As a result, living polymerizations show a linear relationship between polymer chain length and time. The halide compound to be used herein is a compound capable of providing a halide anion. Non-limiting examples of such compounds are NaCl, NaBr, KCl, KBr, $MgCl_2$, $MgBr_2$, $CaCl_2$, HCl, HBr, LiCl, LiBr, $CaBr_2$, as well as

combinations thereof. Halide compounds may disassociate in the reaction composition, generating halide anions which may form complexes with and/or bind to catalysts in solution, resulting in an increased concentration of catalyst/ligand-X (X is the halide anion) complexes which are responsible for end-capping, and thus deactivating, propagating surface polymer chain-end radicals to deliver alkyl halides. Consequently, the number of propagating surface polymer chain-end radicals at any given time is lowered, which may result in at least the following effects, (1) a lowering of the rate with which polymer molecules grow initially due to a lower number of propagating chains, and (2) a lowering of the rate with which chain termination between two propagating polymer molecule chain-end radicals occur (through recombination or disproportionation), leading to an increased living character of the polymerization. In an embodiment, the catalyst is Cu, the ligand is Me_6TREN, PMDETA, TREN, HMTETA, TMEDA, or Me_4Cyclam and the halide compound is NaCl.

The reaction composition for surface polymer formation may further be pH controlled. That is, an acidic or alkaline substance may be added one or more times to the reaction composition prior to or during surface polymer formation. The pH of the reaction composition may depend on acid dissociation constant of the complex formed between the catalyst and the ligand complexes. pH control is described further in WO 2024 155981, which is incorporated herein by reference. To meaningfully determine pH and/or pK_a, the reaction composition may in general be aqueous, i.e., meaning that water is present in a certain amount. Since the catalyst/ligand complexes mentioned herein are basic, the term pK_aH is used, which refers to the pK_a of the conjugate acid. The higher the pK_aH value, the stronger the base. For species which may be protonated more than once pK_aH_1 refers to the pK_a of the conjugate acid obtained after the "first" protonation, and pK_aH_2 refers to the pK_a of the conjugate acid obtained after the "second" protonation; pK_aH_1 is in this case always higher than pK_aH_2, i.e., $pK_aH_1 > pK_aH_2$. Specific pK_a and pK_aH values may be calculated using known titration methods, or, where available, be looked up in various publications and handbooks. Non-limiting examples of alkaline substances are potassium hydroxide (KOH), lithium hydroxide (LiOH), tripotassium phosphate (K_3PO_4), sodium carbonate (Na_2CO_3), or sodium ethoxide (CH_3CH_2ONa). Non-limiting examples of acidic substances are methanesulfonic acid (MSA), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), 2,2,2-trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (pTSA), and nitric acid (HNO_3).

The formed surface polymer may be cross-linked. "Chains" of surface polymers on the surface of the substrate may be cross-linked via several pathways, depending on their structure and chemical functionalities. Generally, a cross-linking molecule must be able to either react at least with two reactive groups present in the polymer molecules, or, be able to react at least once with reactive groups present in the surface polymer and generate in this reaction at least one new reactive group, which may react further with neighboring chains of the surface polymer, leading to cross-linking. As an example of the latter, poly(glycidyl methacrylate) (PGMA) contains a reactive oxirane(epoxide)-moiety, which upon reaction with a nucleophile (Nu) yields a hydroxyl group, and a carbon-Nu covalent bond. The formed hydroxyl group may itself be considered a nucleophile and can react with another oxirane moiety of a neighboring polymer molecule, resulting in formation of a carbon-O covalent bond, which is responsible for the cross-linking of two chains of surface polymers. Suitable nucleophiles for reaction with PGMA include but are not limited to amines, thiols, hydroxyls. Examples of nucleophiles which may react only once with PGMA surface polymer chains include alcohols such as ethanol and phenol, secondary amines such as diethylamine, and thiols such as 1-decanethiol. Examples of nucleophiles that may react at least twice with PGMA surface polymer chains include primary amines such as allyl amine and propyl amine, diamines such as 1,2-diaminoethane, diols such as ethylene glycol and bisphenol A, and dithiols such as ethylene bis(thioglycolate). Cross-linkers which may react e.g. at least three times can be conceptualized by e.g. branched triamines such as propane-1,2,3-amine, and glycerol. In order for a molecule to cross-link chains of surface molecules that contain nucleophilic functional groups such as hydroxyls and amines, the cross-linker molecule should comprise at least two reactive electrophilic sites. Examples thereof include di-acid halides such as succinyl chloride, adipoyl chloride, fumaryl chloride and azealoyl chloride, or dicarboxylic acids such as maleic acid, glutaric acid, and terephthalic acid, which may be activated by suitable reagents such as carbodiimides like 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, diisopropylcarbodiimide, or N,N'-dicyclohexylcarbodiimide, or acid halide forming species such as thionyl chloride.

A reaction composition as defined above may be applied for forming the surface polymer. As mentioned above, the reaction composition may comprise a monomer, a catalyst, a ligand, an activator, and a solvent. The catalyst may be selected from the catalysts defined above. In particular, the catalyst may be obtained from Cu, Fe, or Ru. The reaction composition to be applied in the method may comprise a ligand as defined above. In particular, the ligand may be selected

from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethyl-amino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethyl-ethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cy-clam), and/or 2,2'-bipyridyl (BiPy). The reaction composition to be used in the method may comprise an activator. Suitable activators may be oxygen scavengers as defined above. In particular, the activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose, glucose with glycose oxidizing enzyme (GO_x), and/or pyrogallic acid. The reaction composition to be used in the method may further comprise a buffer. Suitable buffers are defined above. The reaction composition to be used in the method may further comprise a halogen salt (metal halide). Suitable halogen salts are defined above. The reaction composition to be used in the method may comprise a surfactant. Suitable surfactants are defined above.

The reaction composition may suitably comprise at least one solvent as defined above. The solvent may be any solvent that provides sufficient solubility of the components of the reaction composition. Suitable solvents include, but are not limited to, alcohols (for example, methanol, ethanol, and isopropanol), dipolar aprotic solvents (for example, tetrahydrofuran (THF), methyl acetate, ethyl acetate, butyl acetate, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF)), methylene carbonate, ethylene carbonate, propylene carbonate, ethyl lactate alcohol, toluene ionic liquids, supercritical CO_2, and water, as well as mixtures thereof.

For forming surface polymers, the substrate and the reaction composition as defined herein are typically kept in contact with each other for a suitable period (residence time), such as from 30 seconds to 5 hours. The residence time includes, but is not limited to 30 seconds, 1 minute, 5 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. The surface polymer formation may take place at ambient temperature (room temperature), or with cooling or heating. Suitable temperatures are such from 20°C up to 120 °C, such as from room temperature (approximately 20°C) to 120°C. Specific temperatures include, but are not limited to, 20°C, room/ambient temperature (approximately 20°C), 30°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, and 120°C. The residence time and temperature during the residence time may suitably be computer controlled. Following formation of surface polymers, the substrate may be subjected to a rinsing and cleaning process, typically flushing with a suitable solvent, sonicating, and/or drying. The

substrate onto which surface polymers are to be formed may be brought into contact with the reaction composition by immersing the substrate into the reaction composition, or by spraying or painting the reaction composition onto the substrate. Polymerization times may depend on the kinetics of the polymerization, the monomer used, the catalyst/ligand complex used and further on the type of substrate. Other ways of adjusting residence time and temperature may be based on conditions in the compartment holding the reaction composition (bath conditions) and/or measurements.

It is to be understood that the components of the reaction composition, which are needed for forming surface polymers, may be provided as discrete components to be mixed before surface polymerization, or may be pre-mixed and activated for surface polymerization shortly before the surface polymerization, that is, the monomer, the solvent, the catalyst/ligand complex are premixed and the catalyst activator is added shortly, usually within 5 minutes, before surface polymerization.

The substrate may be rinsed one or more times following surface polymer formation. Suitable rinsing may include flushing the substrate with different solvents (such as acetone, water, ethanol or combinations thereof), optionally in combination with sonication.

Surface polymers formed on a substrate may be analyzed, e.g., by ellipsometry. Ellipsometry provides a measurement of the average dry film thickness of the surface polymer across the substrate or a portion of a substrate. Generally speaking, a substrate with a surface polymer (for ellipsometry) is herein considered dry when no visible solvent film, droplets, or residues are observed with the naked eye on the surface of the substrate. Other methods of obtaining a dry substrate may be used, some of which include: withdrawal of the substrate(s) from the reaction composition, followed by rinsing by sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes, and drying in ambient air (ambient temperature, ambient pressure) 1-30 minutes. In some cases, the substrates may be flushed with acetone after withdrawal from the reaction composition, followed by air-drying in an oven at 80°C for 15 minutes. Still, in some cases, the substrate(s) may be flushed with acetone, then sonicated in acetone for 5 minutes and left to dry at 80°C for 10 minutes. Alternative, the substrate(s) may be flushed with iPrOH, then sonicated in iPrOH for 5 minutes and left to dry under nitrogen flow for 10-30 minutes.

Within the scope of the present disclosure, the surface polymer layer may possess specific properties obtained through copolymers as described above. The individual components (different monomers) of the copolymers may contribute different properties resulting in a surface polymer with a combination of desired properties. Surface polymer layer can be applied or formed by repeating the polymerization procedures described above to build up copolymers. The same or different monomers can be applied relative to the monomers used to form previous layers. Forming additional layers of surface polymer can be repeated multiple times to obtain a more complex or thicker surface polymer. Surface polymers can also be formed using two or more different monomers grown from one type or different types of initiators thereby forming random or mixed surface polymers, respectively. Hence, two or more functional groups (e.g., halogen atoms, hydroxyl groups, or amine groups) can be incorporated, resulting in surface polymers with a unique set of combined properties, each of which is inherent from individual monomers.

The surface polymer may be a polymer brush. Polymer brushes are upright polymers formed through propagating monomeric units extending the polymer chain from the polymerization initiators on the surface of the substrate.

As used herein, the terms "a substrate" and "the substrate" are intended to include both a single substrate and a plurality of substrates in any form and shape.

Surface polymers may suitably be formed on a portion of a substrate or on all surfaces available on a substrate, that is, surface(s) or portions of surfaces with polymerization initiators attached. Surface polymers may be formed on available surfaces at the same time (e.g., in the case of single-piece substrates) or on available surfaces in a sequential manner (e.g., in the case of fibers, threads, wires etc.).

The polymer may be deposited on the substrate decorated with surface polymers. Non-limiting examples of deposition methods include doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating. These techniques are well known in the art.

The doctor blading technique is shown schematically in Fig. 2 and Fig. 3. In Fig. 2, the first two illustrations show a substrate decorated with surface polymers 100 fastened to a supporting surface

(not shown) using a line of tape 110, the third illustration shows a solubilized polymer deposited onto the substrate 120, and the fourth illustration shows the substrate 120 in the third illustration after removal of the doctor blading tape 110. Fig. 3 is a schematical representation of the doctor blading procedure. In Fig. 3, a substrate is taped onto a supporting surface (not shown) and a knife is dragged across the substrate after depositing the solubilized polymer. The substrate may, following the doctor blading procedure, be subjected to a post-treatment procedure, such as drying, UV curing, and/or post-baking (annealing).

The spin coating technique offers the possibility of depositing a layer of polymer (thin film) on a substrate. A suitable amount of polymer, solubilized in a solvent, is applied at the center of the substrate, followed by a spin at low speed, or, depending on the solubilized polymer, not spun at that stage. Subsequently, the substrate is subjected to a spinning procedure, which may vary depending on the substrate and the polymer. Typically, the spinning is performed at up to 10,000 RPM, optionally in several stages, causing the solubilized polymer to distribute across the substrate, with excess solubilized polymer spinning off the edges. The spin coating procedure is continued until the desired thickness of the polymer film is obtained. See, e.g., "Fabrication and Properties of Spin-Coated Polymer Films" (https://www.researchgate.net/publication/307586194_Fabrication_and_Properties_of_Spin-Coated_Polymer_Films).

The spray coating technique involves spraying a thin film of polymer onto a surface. The technique allows for quick coating of the polymer in question. The polymer is provided in solubilized or sufficiently dispersed form to suit the purpose and the spray equipment. The spray coating technique offers depositing a polymer film on one or more surfaces specifically.

The dip coating technique involves immersing the substrate into a polymer solution and slowly extracting the substrate to coat the surface of the substrate. Usually, care will be taken to ensure the polymer solution has certain properties with regard to viscosity, surface tension, and adhesion.

The flow coating technique involves applying the polymer solution to the surface of the substrate. The polymer solutions is flowed between the substrate and a stationary knife by the force of gravity (capillary effect) or optionally using a spray gun. In general, the technique offers the possibility of depositing thinner polymer films with a high degree of precision.

The physical vapor deposition technique involves the formation of thin polymer films by vacuum evaporation of the polymer. Some polymers undergo random scission of the polymer backbone generating smaller fragments of polymers. Such may be vaporized by thermal agitation and be able to condense as a polymer film on the substrate. Thus, the deposited polymer consists of smaller polymer molecules than the original polymer source. See, e.g., Jpn. J. Appl. Phys. 64 030802 2025.

The comma coating technique involves deposition of a thin film of a polymer on a substrate moved through a gap created by a comma roller and a back roller. The method is suited for polymer solutions with medium to high viscosity, and produces polymer films of medium thicknesses, usually in the micron scale range.

The slot-die coating technique involves depositing of a polymer solution, polymer slurry, polymer hot-melt, or extruded polymer thin film on the substrate by a coating head. The polymer is typically delivered from the coating head either dissolved or suspended in a solvent suited for the particular polymer. The rate of deposition may be controlled by adjusting the viscosity of the polymer solution and the speed of application/movement of substrate. Thus, the thickness of the polymer deposited may be controlled from nanometer range to hundreds of micrometer range.

The polymer to be deposited may be made from any polymerizable monomers as mentioned above. The choice of the polymer for deposition may depend on the intended application. Non-limiting examples of polymers for deposition includes poly(acrylic acid) (PAA), poly(amic acid), poly(methyl methacrylate) (PMMA), polyimide (PI), polyvinylidene fluoride (PVDF), styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC) and polyurethane (PU). Poly(amic acids) are a class of polymers that are generally formed through a polycondensation reaction between a dianhydride and a diamine. The poly(amic acids) are recognized as an intermediate polymer in the formation of polyimides.

In an aspect of the present disclosure, a device stack may be provided, the device comprising a substrate with a first surface, a surface polymer on at least a portion of a first surface covalently attached to the substrate via polymerization initiators covalently attached to the substrate, and a deposited polymer covering and adhering to at least a portion of the surface polymer. The device stack may be represented by Fig. 1, where the device stack comprises substrate 130 surface

polymers 140 bonded to the substrate surface, and a polymer 170 deposited over the surface polymer decorated substrate.

The deposited polymer may be a thin film of polymer material. The term "thin film" is intended to include a polymer film which has a sufficient thickness to suit the intended application. The thin film may generally have a thickness in the range from less than 1 nm up to several microns, such as 30 μm. When the intended application includes electronics, the thin film may have a thickness of up to several microns. When the intended application includes Extreme Ultraviolet lithography (EUV), the thin film may have a thickness in the range of less than 1 nm and up to approximately 10 nm. When the intended application is semiconductor applications, the thin film may have a thickness in the range of less than 1 nm and up to approximately several microns. However, when the intended application is formation of anode layers in electrochemical cells, e.g., thin film batteries, the film may go beyond what is usually understood to be "thin films" and may have a thickness of up to 30 μm. The thin film thickness may be determined using methods usually applied within the relevant field of application.

The substrate of the device stack may be any of the substrates mentioned above. Non-limiting examples include substrates of silicon, copper, glass, ceramic and/or steel.

The polymer of the device stack may be deposited by the techniques mentioned above, e.g., doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

The surface polymer of the device stack may comprise repeat unit of the monomers as mentioned above, e.g., poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(methacrylate) (PMAA), poly(methyl methacrylate) (PMMA), poly(glycidyl methacrylate) (PGMA). The polymer of the device stack may be those mentioned above, e.g., poly(acrylic acid) (PAA), poly(amic acid), and poly(methyl methacrylate) (PMMA).

The surface polymer comprises poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), or poly(glycidyl methacrylate) (PGMA), and the polymer is poly(methyl methacrylate) (PMMA), or poly(amic acid).

A specific example of a device stack may be such, wherein the surface polymer is poly(methyl methacrylate) (PMMA), and the polymer is poly(methyl methacrylate) (PMMA).

The surface polymer of the device stack may be formed by providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate, and exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate. The reaction composition for forming the surface polymer is described above and may in addition to the monomer include a catalyst, a ligand, an activator, and a solvent as described above.

Thus, the device may be prepared by a method comprising providing the substrate, wherein surface polymers are present on at least a portion of the surface of the substrate, providing a polymer, and depositing the polymer on the surface of the substrate to provide an adhering interface between the surface polymer and the polymer.

The deposited polymer may be a thin film of polymer material. The polymer may be provided solubilized in a solvent. The polymer may be deposited by, for example, doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating. After the depositing of the polymer, the device stack may be dried, UV cured, and/or post-baked (post-baking may also be referred to as annealing). The procedures are described above.

In an embodiment, the present disclosure relates to substrates decorated with surface polymers having a deposited film of a polymer for use as a resist suitable for exposure by electron beam lithography or high energy photolithography, such as Extreme Ultraviolet (EUV) Lithography; one example of such a polymer film suitable for use as a resist is PMMA, which may be deposited on to a surface polymer decorated substrate, as described herein. The surface polymer may function as an adhesion layer for the polymer film (resist). The surface polymer may also function to provide a surface with uniform properties enabling deposition of continuous, uniform, very thin – 5 to 20 nm, for example – films by the polymer film deposition processes discussed herein. Such film stacks on a substrate may be represented by Fig. 1, where the structure comprises a substrate

130, surface polymers 140 on a surface of the substrate, and a deposited polymer film 170 functioning as a resist.

In an embodiment, the present disclosure relates to substrates decorated with surface polymers having a deposited film of a polymer for use in electronic devices or semiconductors. "Electronic devices" or "semiconductors" is intended to broadly cover devices that operate by controlling electron flow. These devices may include circuit elements such as, for example, capacitors, resistors, transistors, and/or metallic connections arranged or coupled together to serve a function, and includes integrated circuit (IC) die (microprocessor, memory, etc.), substrate devices (e.g., Printed Circuit Board (PCB), ceramic/organic substrate, etc.) configured to electrically and/or mechanically connect the IC die to other circuits/structures, a die-substrate assembly - that is, a die attached to a substrate (or a) using any known assembly technology (e.g., wire bond, flip chip, overmold or encapsulation, etc.), die-substrate assembly attached to another substrate (e.g., a die-substrate assembly attached to, e.g., a PCB using wire bonds, Ball Grid Arrays (BGA), etc. Electronic devices also include optical display devices that operate using light, lasers, etc. Electronic devices perform a wide range of functions such as controlling other electronic devices, performing high-speed calculations, transforming sunlight to electricity, and transmitting and receiving electromagnetic signals, among other things. Electronic devices are found in the fields of entertainment, communications, power conversion, networks, computers, consumer products, military applications, aviation, industrial controllers, office equipment, automotive, and aerospace. Electronic devices usually contain active and passive electrical structures where active electrical structures include bipolar and field effect transistors that control the flow of electrical current. A transistor either promotes or restricts the flow of electrical current by varying doping levels and application of an electric field or base current. Passive electrical structures, such as resistors, capacitors, and inductors, create a relationship between voltage and current necessary to perform a variety of electrical functions. Both active and passive electrical structures are electrically connected to form integrated circuits that enable electronic devices to perform high-speed calculations and other useful functions. Semiconductor or electronic devices may generally be manufactured using a front-end process, a back-end process, and a packaging process. All three general processes may potentially involve hundreds of steps where a wafer containing a plurality of semiconductors or dies may be layered or inserted with dopants such as phosphorous, arsenic (N-type), and boron (P-type) among other materials or metals through a photomask, an ion implantation, a thermal annealing process, a diffusion, metal and other material depositions,

photolithography-based patterning, an etching process, wet and dry cleaning, etc. The layers on the plurality of semiconductors may be interconnected to each other through vertical interconnections, such as vias and contacts, or through lateral interconnections, such as metal lines. The final layers on the plurality of semiconductors' surfaces on the wafer may include bond pads to electrically connect the respective semiconductors' I/Os to a package substrate or another semiconductor or die. Fabrication methods that are analogous to those described for the front-end process (deposition, patterning, etching, planarization, cleaning, etc.) are utilized. Bumps, wires, conductive pastes, and/or other electrical connection mechanisms may be used to establish the electrical contact between the semiconductor device and the substrate, die, or lead frame of a package. In some embodiments, a metallic pad, or an under-bump metallization (UBM), may be located between the bump and the bond pad where the UBM may contain an adhesion layer, a barrier layer, and a wetting layer. The final packaging process integrates such semiconductor chips/dies onto substrates using, for example, interposers.

Most electronic device systems include a printed circuit board (PCB) with interconnections. A PCB may be a composite of organic and inorganic materials with external and internal wiring that may allow semiconductor devices to be electrically interconnected and mechanically supported. PCBs may largely be made of epoxy-glass-based laminates, ceramic materials, and or metallic materials. PCBs may be sequentially built up through the addition of layers of circuitry over layers of dielectrics and through selectively removing the dielectrics to form micro vias, blind vias, and plated through hole connections. PCBs may include flexible-circuit carriers that may be printed circuits deposited on a flexible dry film. The flexible dry films may predominantly be polyimide and polyester-based materials. In addition, PCBs may have a base material made from a metal, on which glass or polymer may be deposited as insulators and conductive paste, or from thin-film metal, for electrical conduction. The layers of the PCB may include discrete passive components which may reduce or eliminate the number of components mounted on the surface of the PCB 2-dimentionally. This, in turn, reduces the footprint of the chip and reduces the conduction paths and overall capacitance, resulting in reduction of the RC effect for a faster chip response. Such an effect will be maximized (even from volume perspectives), if thin film forms of passive components are integrated within the PCB layers "vertically" (i.e, within the chip area). In such cases, additional interfaces between different materials are formed, as films of material are deposited; these interfaces may benefit from inclusion of polymer brush for enhancing adhesion and other interface-specific properties.

The electronics and semiconductor industries use polyimide (PI) and polyamide (PA), or a combination of PI and PA, which are deposited as films and thin films in device stacks and chip packages. The adhesion of PI/PA polymer materials, deposited as thin films and films, to substrates, may be improved by the presence of a surface polymer, as defined herein, on the substrate. The electronic or semiconductor device may be represented by Fig. 1, where the device comprises an electronic device/semiconductor substrate surface 130, surface polymers 140 bonded to said substrate surface, and a PI/PA polymer material 170 deposited over the surface polymer decorated substrate.

In an embodiment, the present disclosure relates to components of a battery as well as the battery itself.

In general, a battery comprises the following components: a positive electrode current collector; a positive electrode active material; a separator or a solid electrolyte; a negative electrode active material; and a negative electrode current collector. The current collectors are usually an aluminum foil in respect of the cathode, and a copper foil in respect of the anode. Other battery components are outer casing and sealing components.

The current collectors fulfill vital functions within battery systems. They support the electroactive layer (current collectors and active materials) by serving as a substrate for the casting of slurry, a mixture containing one or more active materials, one or more polymers (polymeric binders), and one or more conductive additives. Furthermore, the current collectors facilitate electron flow between the electrode materials and the external circuit.

However, most known batteries have certain drawbacks and/or deficiencies. These can include low cycle life, low energy density, low power density, slow charge rate, poor charge retention or high self-discharge, expansion, high cost, "memory effect," and the need for protection from overcharging and complete discharging. The electrochemical energy storage industry continues to seek technologies that improve the capabilities and performance of electrochemical energy storage devices and provide solutions for one or more of these problems.

In accordance with an aspect of the present disclosure, the positive electrode current collector, the negative electrode current collector, and the separator may be decorated partially or fully with surface polymers. The principle is illustrated in Fig. 19 which schematically shows battery components (positive electrode current collector 1908, negative electrode current collector 1901, and separator 1904) decorated with surface polymers 1903, 1905, 1907.

In an embodiment, the positive electrode current collector may be decorated partially or fully with surface polymers and adhered through the surface polymers to the positive electrode active material. In an embodiment, the negative electrode current collector may be decorated partially or fully with surface polymers and adhered through the surface polymers to the negative electrode active material. In an embodiment, the separator may be decorated partially or fully with surface polymers to provide improved properties of the battery and improved adhesion to the positive electrode active material and/or the negative electrode active material.

In an embodiment, the positive electrode current collector and the negative electrode current collector are a foil of a metal. The foil may suitably be a foil of aluminum, copper or stainless steel. In an embodiment, the negative electrode current collector is a copper foil. In an embodiment, the positive electrode current collector is an aluminum foil.

In an embodiment, the negative electrode active material comprises a polymer (polymeric binder). The polymeric binder is adhered to the negative electrode current collector through the surface polymers. In one embodiment, the polymeric binder is selected from polyacrylic acid (PAA), polyvinylidene fluoride (PVDF), styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC) and polyurethane (PU).

In an embodiment, the surface polymer is poly(tert-butyl methacrylate) (PtBMA) or poly(methacrylic acid) (PMAA).

In accordance with an aspect of the present disclosure, the positive electrode current collector, the negative electrode current collector, and/or the separator may be decorated partially or fully with surface polymers. In an embodiment, the negative electrode active material comprises silicon.

In accordance with an aspect of the present disclosure, a method for forming a positive electrode current collector decorated with surface polymers may comprise: providing a positive electrode current collector; forming polymerization initiators on at least a portion of at least one surface of the positive electrode current collector; and bringing the positive electrode current collector into contact with a reaction composition to form surface polymers from the polymerization initiators.

In accordance with an aspect of the present disclosure, a method for forming a negative electrode current collector decorated with surface polymers may comprise: providing a negative electrode current collector; forming polymerization initiators on at least a portion of at least one surface of the negative electrode current collector; and bringing the negative electrode current collector into contact with a reaction composition to form surface polymers from the polymerization initiators.

In accordance with an aspect of the present disclosure a method for forming a positive electrode current collector decorated with surface polymers adhered to a positive electrode active material may comprise: providing a positive electrode current collector; forming polymerization initiators on at least a portion of at least one surface of the positive electrode current collector; bringing the positive electrode current collector into contact with a reaction composition to form surface polymers from the polymerization initiators; and bringing the positive current collector into contact with a positive electrode active material to adhere the positive electrode active material to the positive electrode current collector through the surface polymers on the surface of the positive electrode current collector.

In accordance with an aspect of the present disclosure a method for forming a negative electrode current collector decorated with surface polymers adhered to a negative electrode active material may comprise: providing a negative electrode current collector; forming polymerization initiators on at least a portion of at least one surface of the negative electrode current collector; bringing the negative electrode current collector into contact with a reaction composition to form surface polymers from the polymerization initiators; and bringing the negative current collector into contact with a negative electrode active material to adhere the negative electrode active material to the negative electrode current collector through the surface polymers on the surface of the negative current collector. In embodiments the negative electrode active material is in the form of a slurry when brought into contact with the positive electrode current collector, wherein the slurry

includes a polymer (polymeric binder), and calendaring and baking processes may be applied subsequently.

In accordance with an aspect of the present disclosure, the substrate is silicon material decorated with surface polymers, where the silicon material is in the form of particles, chunks, etc., distributed throughout the negative electrode active material, which material is bound together by a polymer (polymeric binder). The polymeric binder is adhered to the silicon through the surface polymers on the surface of the silicon. In one embodiment, the polymeric binder is selected from, but not limited to, polyacrylic acid (PAA), polyvinylidene fluoride (PVDF), styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC), polyimide and polyurethane (PU). In an embodiment, the surface polymer is poly(tert-butyl methacrylate) (PtBMA) or poly(methacrylic acid) (PMAA).

Positive electrode active materials include lithium-composites (e.g., lithium-containing metal oxides, including lithium cobalt oxides (LCO); lithium manganese oxides (LMO); lithium iron phosphates (LFP); lithum manganese iron phosphates (LMFP); lithium manganese phosphate (LMP); lithium nickel manganese oxide (LNMO); lithium nickel-cobalt-aluminium oxide (NCA); lithium-nickel manganese cobalt aluminium oxides (NMCA); and lithium nickel manganese cobalt oxides (NMC)). For sodium-ion (Na-ion) cells, positive electrode active materials may be analogous to Li-ion, for example, sodium manganese oxide (NMO) and sodium iron phosphate (NFP). Other appropriate positive electrode (cathode) active materials can comprise metal hydride in nickel-metal hydride (Ni-MH); sulphur in sodium-sulphur (Na-S) and lithium-sulphur (Li-S); PbO_2 in lead-acid (Pb-acid); air/oxygen in metal-air battery types. Metals in metal-air/oxygen battery types can for example comprise zinc, lithium, manganese, aluminium, and/or sodium. Other positive electrode active materials known in the art can be employed in embodiments of the present disclosure.

Negative electrode active materials may comprise graphite. Negative electrode active materials may further comprise graphene; carbon nanotubes (CNT); various metals, e.g., titanium (Ti), silicon (Si), and various Si-derivatives such as silicon oxide (SiO_x), silicone oxynitrides (SiO_xN_y), and silicon nitride (SiN_x); germanium (Ge); tin (Sn); antimony (Sb); iron (Fe); zinc (Zn); sodium (Na); cobalt (Co); nickel (Ni); manganese (Mn); copper (Cu); chromium (Cr); molybdenum (Mo);

various metal oxides, e.g., lithium titanate (LTO), and metal nitrides, e.g., $LiMoN_2$, and $NiCo_2N$; as well as mixtures thereof.

The separator may comprise a porous film of organic polymers, e.g., polyethylene (PE); polypropylene (PP); polyimide (PI) polyamide (PA); polyvinyl chloride (PVC); polytetrafluoroethylene (PTFE); polyvinylidene fluoride (PVDF); poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP); polyvinyl alcohol (PVA); polyvinyl butyral (PVB); polyethylene glycol (PEO); polyacrylonitrile (PAN); combinations thereof; natural fiber materials such as cotton and cellulose; solid-state electrolytes such as LLZO and sulfur-based materials; inorganic ceramics such as SiO2, Al2O3, MgO, or a combination of organic polymers coated with inorganic ceramics or an organic polymer filled with ceramic nanoparticles.

A battery may further comprise an additive. The additive may be disposed on the positive electrode current collector, the positive electrode active material, negative electrode current collector, the negative electrode active material, or some or all of these, or permeate, in liquid case, through the separator. Suitable additives include but are not limited to carbon black and graphene and electrolyte additives such as vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), trifluoropropylene carbonate (TFPC), 2-cyanoethyl triethoxysilane (TEOSCN), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalate)borate (LiDFOB), and lithium fluoromalonato(difluoro)borate (LiFMDFB).

In an aspect of the present disclosure a system is provided. Fig. 25 is a non-limiting schematic illustration of a system for forming surface polymers on at least a portion of a substrate. The system comprises a reaction composition container 2504 containing the aforementioned reaction composition 2505. Container 2504 may relate to any vessel or chamber suitable for holding the reaction composition. At least a portion of a polymerization initiator-modified substrate 2502 is brought into contact with the reaction composition 2505, for example by at least partly immersing a desired surface of substrate 2502 into the reaction composition, thereby enabling surface polymers to form on the substrate.

Optionally, the system of Fig. 25, may comprise one or more further containers, each container comprising different compositions and/or agents for treating the substrate 2502, either prior to the substrate being brought into contact with the reaction composition 2505, or afterwards. Where

substrate 2502 has not been pre-treated with a polymerization initiator, then the system may further comprise a container 2506 holding a polymerization initiator chemistry 2507, thus, forming the polymerization initiator-modified substrate 2502 in the container 2506.

Fig. 25 may relate to embodiments in which the substrate has been pre-coated with a polymerization initiator. In such embodiments, and as illustrated in Fig. 25, a cleaning container 2514 may be provided, comprising a cleaning agent or cleaning device 2516. The cleaning agent/device 2516 may be used to clean the surface of substrate 2502 prior to bringing it into contact with reaction composition 2505 held by the reaction composition container 2504. This may be achieved by, at the very least, subjecting at least a portion of the substrate 2502 on which it is desired to form surface polymers on, to cleaning procedures in container 2514 using cleaning agent/device 2516. In this way, any impurities which may interfere with the formation of the surface polymers, are removed from the surface of substrate 2502, prior to bringing substrate 2502 into contact with the reaction composition 2505. The system may additionally include a substrate displacement device 2503 for bringing the substrate 2502 at least partly into contact with the reaction composition 2505 held by the reaction composition container 2504 for a controlled time to ensure surface polymers form. The displacement device 2503 may be used to remove the substrate 2502 from the reaction composition 2505 following surface polymer formation. Thus, the substrate displacement device 2503 may be configured to maintain the surface of substrate 2502 at least partly in contact with the reaction composition 2505 to enable surface polymers to form on at least a portion of the surface of the substrate, and the substrate displacement device 2503 may be configured to maintain the substrate 2502 in contact with the reaction composition 2505 for a predetermined amount of time.

In embodiments where the system of Fig. 25 may comprise two or more containers, in addition to bringing substate 2502 into contact with the compositions contained by each container, the substrate displacement device 2503 is configured to transport substrate 2502 to and from each container. For example, as illustrated in Fig. 25, the substrate displacement device 2503 is configured to first transport substrate 2502 into contact with cleaning agent/device 2516 in container 2514, and/or a polymerization initiator composition 2507 if the substrate is not pre-coated with a polymerization initiator as mentioned previously, held in the polymerization initiator container 2507, and subsequently to transport the substrate 2502 from the polymerization initiator container 2507 to the reaction composition container 2504, where the substrate is brought at least

partly into contact with the reaction composition 2505 held by the reaction composition container 2504. In the latter example, the substrate may in embodiments be cleaned between initiator coating and surface polymer formation.

The substrate displacement device 2503 may relate to any device capable of transporting the substrate from one container to another container. For example, the substrate displacement device 2503 may relate to a mechanical device. In particular, it is envisaged that the substrate displacement device 2503 may comprise any one of: a conveyor system; a programmable mechanical arm; and/or a roll-to-roll processor/mechanism.

A conveyor system as used herein may refer to a mechanical system that is used to move a material, such as the substrate, which in embodiments may be in a substrate holder on its own or with other substrates, from one process container to another, typically comprising a movable conveyor, powered by a drive system and having a series of rollers or pulleys that support and guide the belt. In use, the substrate may be placed on the conveyor which passes the substrate through the one or more containers comprised in the system. In this way, as the conveyor is powered, the substrate is passed through the component(s) held by each container within the system. Furthermore, in some embodiments the containers are enclosures in which the reaction composition, or other appropriate wet chemistry, is uniformly applied over the substrate using spray nozzles.

In some embodiments a programmable mechanical arm, such as a robotic arm, may be used to transport the substrate, which may be in a holder as described above.

A roll-to-roll processor or mechanism is particularly advantageous for use where the substrate may be flexible and elongated, such as a cable, wire, foil, or any other elongated flexible substrate. Fig. 26 illustrates such an embodiment, in which the substrate displacement device relates to a roll-to-roll processor 2618, comprising a sending roll 2621, a receiving roll 2622 and a plurality of rollers 2620. At least some of the rollers 2620 and the receiving roll 2622 are driven, thereby enabling a flexible elongated substrate 2623 to be passed from sending roll 2621 through the reaction composition 2605 in container 2604 to the receiving roll 2622. The roll-to-roll mechanism can be utilized as a replacement to the substrate displacement device 2503 in Fig. 25 when elongated flexible substrates are being processed.

In yet further embodiments, at least one of the plurality of containers may comprise an annealing oven for annealing the formed surface polymers. In a similar manner as described previously, the substrate displacement device 2503 may be configured to transport the substrate with the formed surface polymers to the annealing oven 2509 and to bring the substrate with surface polymers into position for annealing. The annealing oven is equipped with a heating device for annealing the formed surface polymers and the gas environment 2511 in the oven may be controlled as needed – for example, to avoid oxidation by using only non-oxidizing gasses.

Furthermore, at least one of the plurality of containers may comprise a polymer deposition system. In a similar manner as described previously, the substrate displacement device 2503 may be configured to transport the substrate with the formed surface polymers to the polymer deposition system and to bring the substrate with surface polymers into position for polymer deposition. The polymer deposition system may comprise a doctor blade coater configured to spread the polymer on to the surface polymer, a spin coater configured to spin coat the polymer on to the surface polymer, a comma coater configured to spread the polymer on to the surface polymer, or a slot-die coater configured to spread the polymer on to the surface polymer, a spray coater for spraying the polymer in a volatile carrier solvent on to the surface polymer, a dip coating tank for applying the polymer on to the surface polymer, a flow coating tool for gravity flowing the polymer in a volatile carrier solvent over the surface polymer, or a vacuum chamber configured for physical vapor deposition of the polymer on to the surface polymer.

Furthermore, extra containers may be added as needed for rinsing, etc. between processes. The substrate displacement device may be one or more robots or a conveyor system with the capability to move wafer holders horizontally and vertically in and out of containers and from container to container.

In an aspect of the present disclosure, a system for forming a device stack as described herein is provided, the system comprising a reaction composition container containing a reaction composition, said reaction composition comprising a monomer, a catalyst, a ligand, a catalyst activator, and a solvent, a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time, wherein the controlled time may be sufficient for surface polymers to be formed on the portion of the polymerization initiator-modified substrate,

a polymer deposition system for depositing a polymer at least over a portion of the formed surface polymer, wherein the substrate displacement device may further be configured for bringing the surface polymer coated substrate into the polymer deposition system for a controlled time, and wherein the controlled time may be sufficient for depositing a polymer on a least a portion of the surface polymers, and optionally a device for drying, curing, or post-baking the polymer following the depositing of the polymer. The substrate displacement device may comprise any one of a conveyor system, a programmable mechanical arm, or a roll-to-roll mechanism. The system may further comprise a polymerization initiator container containing polymerization initiator agent, wherein the substrate displacement device may further be configured to bring the portion of the substrate for attachment of polymerization initiators into contact with the polymerization initiator agent to form polymerization initiators at the substrate surface, prior to bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition. The system may further comprise a cleaning container, the cleaning container containing a cleaning agent, wherein the substrate displacement device may be configured to bring the portion of the polymerization initiator-modified substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition, and optionally the substrate displacement device into contact with the reaction composition, and optionally the substrate displacement device may be configured to bring the portion of the substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion into contact with the polymerization initiator. The polymerization initiator container may be a vacuum oven. The polymer deposition system may comprise a doctor blade coater configured to spread the polymer on to the surface polymer, a spin coater configured to spin coat the polymer on to the surface polymer, a comma coater configured to spread the polymer on to the surface polymer, a slot-die coater configured to spread the polymer on to the surface polymer, a spray coater for spraying the polymer in a volatile carrier solvent on to the surface polymer, a dip coating tank for applying the polymer on to the surface polymer, a flow coating tool for gravity flowing the polymer in a volatile carrier solvent over the surface polymer, or a vacuum chamber configured for physical vapor deposition of the polymer on to the surface polymer.

Aspects and embodiments of the disclosure are further illustrated by the following, non-limiting examples.

Examples

Chemicals

Silicon wafers substrates (Test CZ-Si, p-type (boron), thickness 525 ± 25 µm) purchased from MicroChemicals GmbH.

Stainless steel substrates (AISI 304) purchased from Jensen Metal.

ABC clean A200 purchased from ABC-Clean ApS.

Ammonia 25% p.a. purchased from Chemsolute.

Acetone (>99%) purchased from Chemsolute.

(*p*-chloromethyl)phenyltrimethoxysilane (CPTMS) 95% grade purchased from Gelest.

tris[2-(dimethylamino)ethyl]amine (Me_6TREN, ≥98% grade) purchased from abcr or Alfa Aesar.

Isopropanol (iPrOH) 99.8% purchased from ChemSolute.

tert-butyl methacrylate (tBMA) (>98%) monomer purchased from TCI.

Sodium ascorbate (NaAsc) (≥98%) purchased from Sigma-Aldrich.

Methanesulfonic acid (≥99%) purchased from Sigma-Aldrich.

Dichloromethane (99.8) purchased from ChemSolute.

Ethanol (EtOH) (96%) purchased from Kiiltoclean.

Poly(acrylic acid) (PAA) (450 kDa) purchased from Sigma-Aldrich.

Poly(pyromellitic dianhydride-co-4,4′-oxydianiline), amic acid solution (poly(acid acid)) (15 – 16% in NMP) purchased from Sigma-Aldrich.

Electrical insulation tape, Nitto, 228SKA, EN60454-3-1-7/F-PVCp/90.

H_2O_2 (30% in water) purchased from ChemSolute.

Methyl methacrylate (MMA) monomer (>99.9%) purchased from Sigma-Aldrich.

Polymethacrylate polymer (PMMA) (996 kDa) purchased from Sigma-Aldrich.

Polyester tape (Flash tape K 7666 204C, 63 µm) purchased from Haufler Composites GmbH & Co. KG.

Adhesive tape, ISO 2409 & ISO 8502-3, purchased from Elcometer.

Poly(2-hydroxyethyl methacrylate) (HEMA) monomer (97%) purchased from Sigma-Aldrich.

Acrylamide (AAm) monomer (≥98%) purchased from Sigma-Aldrich.

Glycidyl methacrylate (GMA) monomer (≥97%) purchased from Sigma-Aldrich.

Alkyl methacrylate (AMA) monomer (98%) purchased from Sigma-Aldrich.

Cu(OH)2 (≥97.5%) purchased from Carl Roth GmbH + co. KG.

Tris(2-pyridylmethyl)amine (TPMA), (97%), purchased from BLD Pharmatech GmbH.

Copper(II)chloride dihydrate ($CuCl_2$ $2H_2O$) (≥99.0%), purchased from Sigma Aldrich.

Anisole, purchased from Sigma Aldrich.

Equipment

Throughout the examples, DI-water refers to tap water deionized using the deionizing equipment (Silhorko with M22-F softening plant, RO B1-2 Reverse Osmosis plant and Silex 2BS mixed bed plant).The DI-water has a conductivity of <0.5 μS, indicating an ultrapure quality with very low presence of ions. The quality of the DI-water was confirmed at least weekly. DI-water holds a conductivity of less than 0.5 μS, indicating very low presence of ions, below 0.1 mg/L.

Bandelin Sonorex Super RK100 sonicator (35 kHz ultrasound frequency, 80 W nominal ultrasonic power).

Binder model FD 56 oven.

Vacuum oven Faithful Vacuum Drying Oven-DZ-BCII.

Stanley knife for doctor blading (Stanley Utility Blade).

Crosshatch Cutter, Elcometer Model 1542 6 x1 mm.

Dino-Lite Universal microscope.

Example 1

Pre-cleaning of silicon wafers and stainless steel substrates

This example describes a set of procedures for pre-cleaning of substrates for surface polymer formation.

Three different substrate preparation procedures were used for silicon wafer substrates and 50 x 50 x 0.8 mm AISI 304 stainless steel substrates, namely:

Substrate Preparation Procedure A:

Racks containing the substrates were placed in an aqueous solution of ammonia (15 vol% DI-water/85 vol% ammonia) and sonicated for 10 minutes. Then, the substrates were flushed with DI-water and sonicated in DI-water for 10 minutes. Thereafter, the racks containing the substrates were transferred to a 5% solution of ABC clean A200 and sonicated for 10 minutes. This step was followed by flushing the substrates in DI-water and sonicating the substrates in DI-water for 5 minutes. Finally, the substrates were flushed with acetone (>99%, Chemsolute), and left to dry at room temperature (ambient pressure).

Substrate Preparation Procedure B:

An alkaline piranha solution was prepared of 2.5 L DI-water, 500 mL aqueous ammonia, and 500 mL H_2O_2 by pouring aqueous ammonia and H_2O_2 into two separate 500 mL cylinders and adding the contents of the two cylinders into a 5 L container with 2 L boiling DI-water, and another 500 mL boiling DI-water was added. The substrates, placed in a rack, were initially sonicated in iPrOH for 5 minutes. The rack containing the substrates was withdrawn and dried in an oven for 15 minutes at 80°C. 2.5 L of the alkaline piranha solution was poured into a heated sonicator (temperature settings between 60-70°C). The substrates, in the rack, were added (without sonication) and left for 10 minutes in the piranha solution, before being transferred to a container filled with DI-water. The substrates were flushed with DI-water and moved to a fresh solution of DI-water and sonicated for 5 minutes, followed by sonication in iPrOH for 5 minutes. Then the substrates were dried in an oven (Binder model FD 56 oven) for 15 minutes at 80°C.

Substrate Preparation Procedure C:

In this process the substrates were retrieved directly from storage and used in subsequent surface modification steps e.g. deposition of initiator as described in Example 2, without any chemical pre-cleaning.

Example 2

Chemical vapor deposition of (*p*-chloromethyl)phenyltrimethoxysilane (CPTMS)

Two procedures were used for attaching CPTMS to the substrates.

Silicon wafer substrates, and stainless steel substrates, treated as described in Example 1, Substrate Preparation Procedure A, B or C, were used for surface polymerization initiator-modification with (*p*-chloromethyl)phenyltrimethoxysilane (CPTMS) using a chemical vapor deposition method. Two different methods for chemical vapor deposition were used, namely:

CPTMS Procedure A:

The substrates were placed in a rack and placed in a vacuum oven (Faithful) with 16 vials of 100 µL CPTMS (polymerization initiator liquid) at approximately 45°C for 150 minutes. The gauge pressure was lowered to -1.0 bar, whereby the CPTMS evaporated, and the substrates were left for 150 minutes. Thereafter, the substrates were removed and placed in an oven at approximately 80°C

for 5 minutes to anneal the silane polymerization initiator layer. The substrates with polymerization initiator deposited were stored in a sealed, dark box until use.

CPTMS Procedure B:

The substrates were placed in a rack and placed in a vacuum oven (Faithful) with 16 vials of 100 µL CPTMS (polymerization initiator liquid) at approximately 100°C for 30 minutes. The gauge pressure was lowered to -1.0 bar, whereby the CPTMS evaporated, and the substrates were left for 30 minutes. Thereafter, the substrates were removed and left at ambient temperature for 24 hours to anneal the attached silane polymerization initiator layer. The substrates with polymerization initiator deposited were stored in a sealed, dark container until use.

Example 3

Doctor blading procedure

Description of general doctor blading procedure.

To deposit a polymer (solubilized in a solvent) onto a substrate, which may or may not be modified with surface polymers, the substrate is placed flat on a supporting surface and attached to the supporting surface by applying a line of Nitto tape on the left and right-hand sides of the substrate, leaving a doctor blading track (having a height from the substrate equaling the height of the tape; usually about 63 µm). A suitable amount of solubilized polymer (an excess of solubilized polymer is placed to ensure complete coating of the doctor blade track), is then placed at one end of the doctor blading track, and the solubilized polymer is then distributed across the doctor bladed track on the substrate by dragging a blade of a knife (e.g., a Stanley knife blade suited for doctor blading) across the doctor blading track. The process is indicated schematically in Fig. 2 and Fig. 3. In Fig. 2, the first two illustrations show a substrate decorated with surface polymers 100 fastened to a supporting surface (not shown) using a line of tape 110, the third illustration shows a solubilized polymer deposited onto the substrate 120, and the fourth illustration shows the substrate 120 in the third illustration after removal of the doctor blading tape 110. Fig. 3 is a schematical representation of the doctor blading procedure. In Fig. 3, a substrate is taped onto a supporting surface (not shown) and a knife is dragged across the substrate after depositing the solubilized polymer. Note that other methods for coating may be applied, e.g., spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die in place of doctor blading.

Certain types of solubilized polymers may need a post-treatment after the doctor blading to ensure satisfactory properties or to ensure formation of the desired polymer film. Such post-treatments include one of the following:

Post-treatment A:

After doctor blading the solubilized polymer onto the substrates, the substrates are left under ambient conditions (ambient temperature, ambient pressure) overnight, while the solvent evaporates and the film dries up.

Post-treatment B:

Post-treatment B consists of a two-step post-bake (annealing) process following doctor blading. The samples are placed on a heating plate at a temperature of 110°C for 5 minutes and then transferred to a second heating plate at a temperature of 175°C, for 60 minutes.

Post-treatment C:

Following doctor blading of the solubilized polymer, the substrates are left to dry for 4 hours under ambient conditions (ambient temperature, ambient pressure).

Example 4

Spin coating procedure

To spin coat a solubilized polymer onto a substrate, the substrate is placed on the vacuum chuck of the spin coater, and the vacuum is turned on to hold the substrate in place. The substrate is then flooded with an appropriate amount of solubilized polymer (e.g. ~1.5 mL for a quadrant substrate with a side length of 2"). The substrate is then spin coated by accelerating the spin speed to 500 RPM during 1 s, and spinning at 500 RPM for 5 seconds, Then, the spinning speed is increased to a final speed over an 8 second period. The final spinning speed is selected to yield the desired thickness of the spin coated layer and can be varied to control the thickness of the spin coated polymer layer. Generally, the final spinning speed will be in the range from 1,000 to 10,000 RPM.

Example 5

Crosshatch testing procedure

The substrate to be evaluated is placed on a hard surface, and the Elcometer Crosshatch Cutter, equipped with a 6x1mm knife, is placed on the substrate and dragged across the surface in a smooth motion while applying a steady pressure, in order to cut through the deposited polymer to the substrate surface. The substrate to be tested is then turned 90 degrees and the cutting is repeated in a similar fashion, to cut out a grid of 25 1x1 mm^2 squares in the deposited polymer film. Then, a piece of tape (ASTM Standard: ASTM D 3359 Adhesive Tape, Elcometer and ISO Standard: ISO 2409 & ISO 8502-3 Adhesive Tape) is applied to the substrate, and the tape is peeled off, according to the selected standardized testing method (ASTM: the tape is peeled at a 180° angle to the substrate (parallel to the substrate surface), ISO: the tape was peeled at a 60° angle to the substrate surface). Finally, the crosshatch result is scored according to the selected standardized method, as indicated in Fig. 24 (see, e.g., www.defelsko.com/resources/finish-coatings-system-adhesion-and-test-methods). The scoring according to the ASTM and ISO standards, respectively, are interconvertible, as indicated in Fig. 24 and the table below, and thus results from ASTM standardized crosshatch tests can be compared directly to results obtained from ISO standardized crosshatch tests.

Table 1: ASTM and ISO class scoring criteria.

ISO Class: 0/ASTM Class: 5B	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
ISO Class: 1/ASTM Class: 4B	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not significantly greater than 5% is affected.
ISO Class: 2/ASTM Class: 3B	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.
ISO Class: 3/ASTM Class: 2B	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.

ISO Class: 4/ASTM Class: 1B	The coating has flaked along the edges of the cuts in large ribbons, and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65% is affected.
ISO Class: 5/ASTM Class: 0B	Any degree of flaking that cannot even by classified by ISO Class 4/ ASTM Class 1B.

The entire crosshatching procedure is schematically shown Fig. 4. In Fig. 4, the first illustration shows the substrate decorated with surface polymers 200 with the doctor bladed polymer 210; the second illustration shows the crosshatches 220 after cutting; the third illustration shows the substrate after applying the tape 230; the fourth illustration shows crosshatches 240 remaining on the substrate after peeling off the tape 230 and the peeled-off crosshatches 250, 260 after peeling off the tape 230.

Example 6

Procedure for formation of poly(methacrylic acid) surface polymers (PMAA polymer brushes)

Firstly, poly(*tert*-butyl methacrylate) (PtBMA) surface polymers were prepared. In a subsequent procedure, the *tert*-butyl group was removed to reveal the PMAA surface polymer.

To a glass container (container A) was added: 31.2 mL Me_6TREN catalyst solution (prepared from 148 µL tris[2-(dimethylamino)ethyl]amine (Me_6TREN, ligand), 31.05 mL DI-water, and 324 mg/l Cu(II) obtained from a solid copper source), 358 mL DI-water, 537 mL isopropanol, and 75 mL *tert*-butyl methacrylate (tBMA) monomer. In a separate glass container (container B), 4000 mg sodium ascorbate (catalyst activator) was dissolved in 15 mL DI-water. The content of container B was poured into container A, and the reaction composition was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si and stainless steel substrates. Both Si and stainless steel substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C, and functionalized with CPTMS polymerization initiators as described in Example 2 using either CPTMS Procedure A or B. The substrates were left in the reaction composition for 30 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature. The average dry film

thickness of the formed surface polymers was determined by ellipsometry and reported in Table 1.

Table 1. Average dry film thickness of the PtBMA surface polymers.

Substrate ID	Surface polymer thickness (nm)	Standard deviation (nm)
Si-PtBMA-1	70.6	1.4
Si-PtBMA-2	65.3	1.1
Si-PtBMA-3	65.6	2.8
Stainless steel-PtBMA-1	102.3	1.8
Stainless steel-PtBMA-2	103.0	2.0
Stainless steel-PtBMA-3	101.5	1.1

The substrates with PtBMA surface polymers were submerged in a solution consisting of 1.3 mL methanesulfonic acid in 1000 mL dichloromethane for 30 minutes to remove the *tert*-butyl group and reveal the PMAA surface polymers. After 30 minutes, the substrates were removed from the solution and rinsed by sonication for 5 minutes in dichloromethane and 5 minutes in ethanol. Table 2 shows the surface polymer thickness as determined by ellipsometry after removal of the *tert*-butyl group. In line with expectations based on the molecular weight of a repeat unit of tBMA and of a repeat unit of MAA, the average dry film thickness of the surface polymer layer decreased following removal of the *tert*-butyl group which was fully expected and correlated with the measurements.

Table 2. Average dry film thickness of the PMAA surface polymers.

Substrate ID	Surface polymer thickness (nm)	Standard deviation (nm)
Si-PMAA-1	36.1	0.6
Si-PMAA-2	33.3	0.5
Si-PMAA-3	33.2	1.1
Stainless steel-PMAA-1	52.2	1.4
Stainless steel-PMAA-2	53.4	0.5
Stainless steel-PMAA-3	51.7	0.9

Example 7

Procedure for formation of poly(2-hydroxyethyl methacrylate) (PHEMA) surface polymer (polymer brushes)

To a glass container (Container A) was added: 25.0 mg $Cu(OH)_2$, 260.0 mg tris(2-pyridylmethyl)amine (TPMA), and 50 mL DI-water. Container A was capped with a lid and placed in an oil bath at 50°C and stirred for 3 hours. After 3 hours the solution in Container A was sonicated for 5 minutes. To a glass container (Container B) was added: 16 mL of the contents of Container A, DI water (904 mL), and 2-hydroxyethyl methacrylate (74 mL). In a separate glass container (Container C), 3999.9 mg sodium ascorbate (catalyst activator) was dissolved in 15 mL DI-water. The content of Container C was poured into container B, Container B was sealed and shaken to mix the contents, and the reaction composition of Container B was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si substrates. Si substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C and functionalized with CPTMS polymerization initiators as described in Example 2 using Either CPTMS Procedure A or B. The substrates were left in the reaction composition for 20 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature, and the dry film thickness of the surface polymers was determined by ellipsometry. The dry film thickness of the surface polymers on specific substrates is reported in the examples pertaining to crosshatch testing of those substrates, namely in Example 13 and Example 14.

Example 8

Procedure for formation of polyacrylamide (PAAm) surface polymer (polymer brushes)

To a glass container (Container A) was added: 1.6 mL Me_6TREN catalyst solution (prepared from 7.6 µL tris[2-(dimethylamino)ethyl]amine (Me_6TREN, ligand), 1.6 mL DI-water, and 324 mg/l Cu(II) obtained from a solid copper source), 89.4 mL DI-water, and 6000.3 mg acrylamide monomer. In a separate glass container (Container B), 400.3 mg sodium ascorbate (catalyst activator) was dissolved in 1.5 mL DI-water. The content of container B was poured into Container A, and the reaction composition was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si substrates. Si substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C and functionalized with CPTMS polymerization initiators as described in Example 2 using Either CPTMS Procedure A or B. The substrates were left in the reaction composition for 40 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature. The substrates were left to dry at ambient pressure and ambient temperature, and the dry film thickness of the surface polymers was determined by ellipsometry. The dry film thickness of the surface polymers on specific substrates is reported in the examples pertaining to crosshatch testing of those substrates, namely in Example 13 and Example 14.

Example 9

Procedure for formation of poly(allyl methacrylate) (PAMA) surface polymer (polymer brushes)

To a glass container (Container A) was added: 25.0 mg $Cu(OH)_2$, 260.0 mg tris(2-pyridylmethyl)amine (TPMA), and 50 mL DI-water. Container A was capped with a lid and placed in an oil bath at 50°C and stirred for 3 hours. After 3 hours the solution in Container A was sonicated for 5 minutes. To a glass container (Container B) was added: 16 mL of the contents of Container A, DI water (504 mL), ethanol (430 mL), allyl methacrylate (30 mL). In a separate glass container (Container C), 4000.2 mg sodium ascorbate (catalyst activator) was dissolved in 15 mL DI-water. The content of Container C was poured into container B, Container B was sealed and shaken to mix the contents, and the reaction composition of Container B was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si substrates. Si substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C and functionalized with

CPTMS polymerization initiators as described in Example 2 using Either CPTMS Procedure A or B. The substrates were left in the reaction composition for 10 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature. The substrates were left to dry at ambient pressure and ambient temperature, and the dry film thickness of the surface polymers was determined by ellipsometry. The dry film thickness of the surface polymers on specific substrates is reported in the examples pertaining to crosshatch testing of those substrates, namely in Example 13 and Example 14.

Example 10

Procedure for formation of poly(glycidyl methacrylate) (PGMA) surface polymer (polymer brushes)

To a glass container (container A) was added: 13.7 mg $CuCl_2*2H_2O$, 84.3 mg tris(2-pyridylmethyl)amine (TPMA), 7 mL ethanol, and 9 mL DI-water. The contents of Container A were sonicated until dissolved. To a glass container (Container B) was added: 16 mL of the contents of Container A, DI water (484 mL), ethanol (410 mL), glycidyl methacrylate (75 mL). In a separate glass container (container C), 4002.6 mg sodium ascorbate (catalyst activator, commercially available, ≥98% grade from Sigma-Aldrich) was dissolved in 15 mL DI-water. The content of container C was poured into container B, Container B was sealed and shaken to mix the contents, and the reaction composition of Container B was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si substrates. Si substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C and functionalized with CPTMS polymerization initiators as described in Example 2 using Either CPTMS Procedure A or B. The substrates were left in the reaction composition for 20 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature. The substrates were left to dry at ambient pressure and ambient temperature, and the dry film thickness of the surface polymers was determined by ellipsometry. The dry film thickness of the surface polymers on specific substrates is reported in the examples pertaining to crosshatch testing of those substrates, namely in Example 13 and Example 14.

Example 11

Procedure for formation of poly(methyl methacrylate) (PMMA) surface polymer (polymer brushes)

To a glass container (Container A) was added: 16 mL Me_6TREN catalyst solution (prepared from 76 µL tris[2-(dimethylamino)ethyl]amine (Me_6TREN, ligand), 15.924 mL DI-water, and 324 mg/l Cu(II) obtained from a solid copper source), 484 mL DI-water, 410 mL ethanol, and 75 mL methyl methacrylate (MMA) monomer. In a separate glass container (Container B), 4000 mg sodium ascorbate (catalyst activator) was dissolved in 15 mL DI-water. The content of Container B was poured into Container A, and the reaction composition was left 5 minutes to activate the reaction composition for surface polymer formation. The reaction composition was poured into a reaction container with Si substrates. Si substrates were cleaned as described in Example 1 using either Substrate Preparation Procedure A, B, or C, and functionalized with CPTMS polymerization initiators as described in Example 2 using either CPTMS Procedure A or B. The substrates were left in the reaction composition for 40 minutes. The substrates were then withdrawn from the reaction composition and rinsed by dipping in DI-water, and sonication in DI-water for 5 minutes, followed by sonication in acetone for 5 minutes. The substrates were left to dry at ambient pressure and ambient temperature. The substrates were left to dry at ambient pressure and ambient temperature, and the dry film thickness of the surface polymers was determined by ellipsometry. The dry film thickness of the surface polymers on specific substrates is reported in the examples pertaining to crosshatch testing of those substrates, namely in Example 13, Example 14, and Example 15.

Example 12

Adhesion between PMAA surface polymers and PAA polymer

This example demonstrates the impact of a covalently attached poly(methacrylic acid) (PMAA) surface polymer on the adhesion of poly(acrylic acid) polymer.

Preparation of PAA polymer solution

A solution of PAA polymer in DI-water (16.7 wt%) was prepared by adding 10 g of PAA polymer to a glass bottle (100 mL) and adding 50.7 mL DI-water. Hereafter, a stirring magnet was added to the glass bottle, which was then closed with a screw cap lid. The solution was left to stir on a stirring plate (1000 rpm) for 2 days. After 2 days, the resulting solution was sonicated for 15 minutes to remove air bubbles and left again on the stir plate for 1 hour at 500 rpm.

3 unfunctionalized (blank) Si substrates, 3 PMAA surface polymer-modified Si substrates (see Example 5, Si substrates, pre-cleaned as described in Example 1, Substrate Preparation Procedure A, attachment of polymerization initiators according to Example 2, CPTMS Procedure A), 3 unfunctionalized (blank) stainless steel substrates, and 3 PMAA surface polymer-modified stainless steel substrates (pre-cleaned according to Example 1, Substrate Preparation Procedure A, attachment of polymerization initiators according to Example 2, CPTMS Procedure A) were investigated. PAA polymer solution was deposited onto the substrates mentioned by doctor blading (see Example 3, Post-treatment A), and then crosshatch tested as described in Example 5 using the ISO methodology and class scoring as shown in Fig. 24. The deposited PAA polymer film thickness was estimated to be in the range of 20-40 µm (following drying) using a caliper suited for such measurement.

Fig. 5 shows PAA polymer deposited by doctor blading on unfunctionalized (blank) Si substrates. Fig. 6 shows the same substrates as in Fig. 5 after cutting the crosshatches. Finally, Fig. 7 is a microscopic view (Dino-Lite Universal microscopic photograph) of the same substrates as in Fig. 5 after applying and peeling the tape. Evidently, even after just cutting the crosshatches, all the cut squares of PAA delaminate from the blank Si substrates, rendering the tape peel test obsolete, as very miniscule adhesion is obtained between the PAA polymer and unfunctionalized (blank) Si substrates. Thus, it can be concluded that the PAA polymer adheres very poorly to the silicon surface.

Fig. 8 shows PAA deposited by doctor blading onto the Si substrates with PMAA surface polymers. Fig. 9 shows the same PMAA surface polymer-modified substrates after cutting the crosshatches. Finally, Fig. 10 shows the PMAA surface polymer-modified substrates after applying and peeling the tape (Dino-Lite Universal microscopic photographs). Evidently, all the cut squares of PAA remain on the PMAA surface polymer-modified substrates even after the tape peeling test. The crosshatch cutting appeared with very sharply defined edges on the PMAA surface polymer-modified substrates. This indicates a surprisingly strong adhesion promotion of surface polymer-modified substrate and the PAA polymer. It is hypothesized that the PMAA surface polymer provides a surface chemistry favorable for adhesion to the PAA polymer. The inventors ascribe this to strong hydrogen bonding between the carboxylic acids of the PMAA surface polymer and the PAA polymer.

Fig. 11 shows the blank stainless steel substrates after doctor blading with PAA polymer. Fig. 12 shows the substrates after crosshatch cutting. It is noted that the PAA polymer did not adhere completely to the third substrate (marked "3"), whereas this was not observed in the case of the first and second substrates (marked "1" and "2", respectively). The reason for this is presently not known, but as the substrates are unfunctionalized, each substrate may present a different native surface composition. Fig. 13 shows the substrates after applying and peeling the tape. Fig. 14 shows Dino-Lite Universal microscopic photographs of the substrates in Fig. 13. Again, substrate "3" showed markedly poorer adhesion of the PAA polymer. Generally, the better adhesion between the PAA polymer and the blank stainless steel substrates (compared to the blank Si substrates) is to be expected as stainless steel is very polar and so is the PAA polymer.

Fig. 15 shows PMAA surface polymer-modified stainless steel substrates after doctor blading with PAA polymer solution. Fig. 16 shows the substrates after crosshatch cuttings. It is noticed that all squares adhere strongly to the PMAA surface polymer-modified substrate after cutting. Fig. 17 shows the PMAA surface polymer-modified substrates after applying the tape and peeling the tape. The very good adhesion of the squares indicates a strong adhesion between the PMAA surface polymer-modified stainless steel substrate surface and the PAA polymer. Fig. 18 shows Dino-Lite Universal microscopic photographs of the substrates of Fig. 17. As can be seen, all squares are still strongly adhered to the PMAA surface polymer-modified surface of the substrates.

Overall, it can be concluded that modifying the surface of a metal with surface polymers markedly improves the adhesion properties. Thus, it is expected that the improved adhesion will also apply to other types of substrates, like other metals and foils of, e.g., Cu and Al.

Example 13

Adhesion of various surface polymers (polymer brushes) to PMMA polymer

This example demonstrates how certain surface polymers promote adhesion to PMMA polymer which is doctor bladed onto the substrates. The inventors find a correlation between the polarity and structure of the surface polymers and the obtained adhesion, indicated by crosshatch testing according to the ASTM standard scoring system.

A variety of surface polymers were prepared on Si substrates as indicated in Table 3, and adhesion to PMMA polymer was tested for each surface polymer type. Substrate 1-3 in Table 3 are not modified with surface polymers and serve as reference substrates and will be referred to as "blank" substrates. These substrates were cleaned by sonicating in iPrOH for 10 minutes and air dried prior to doctor blading the solubilized PMMA solution. Substrates 4 to 24 were all pre-treated as described in Example 1, using Substrate Preparation Procedure C, and had polymerization initiator (CPTMS) deposited as described in Example 2, CPTMS Procedure B.

Table 3. Si substrates, and surface polymer type of substrate prior to doctor blading pre-treatment prior to doctor blading with PMMA polymer solution. The surface polymer thickness prior to doctor blading with PMMA polymer was determined by ellipsometry (average dry film thickness).

Substrate no.	**Surface polymer preparation Example No.**	**Surface Polymer Type**	**Doctor Blading post-treatment (Example 3)**	**Surface Polymer Thickness**
1	Not applicable	No surface polymer, blank	Post-treatment A	Not applicable
2	Not applicable	No surface polymer, blank	Post-treatment A	Not applicable
3	Not applicable	No surface polymer, blank	Post-treatment A	Not applicable
4	Not applicable	No surface polymer, CPTMS only	Post-treatment A	Not applicable
5	Not applicable	No surface polymer, CPTMS only	Post-treatment A	Not applicable
6	Not applicable	No surface polymer, CPTMS only	Post-treatment A	Not applicable
7	Example 6	PMAA	Post-treatment A	35.2 ± 0.9
8	Example 6	PMAA	Post-treatment A	36.0 ± 1.1
9	Example 6	PMAA	Post-treatment A	36.2 ± 0.9
10	Example 7	PHEMA	Post-treatment A	19.2 ± 0.6

11	Example 7	PHEMA	Post-treatment A	19.2 ± 0.3
12	Example 7	PHEMA	Post-treatment A	19.0 ± 0.3
13	Example 8	PAAm	Post-treatment A	28.0 ± 0.7
14	Example 8	PAAm	Post-treatment A	28.2 ± 0.5
15	Example 8	PAAm	Post-treatment A	28.3 ± 0.6
16	Example 9	PAMA	Post-treatment A	54.7 ± 0.2
17	Example 9	PAMA	Post-treatment A	55.4 ± 0.3
18	Example 9	PAMA	Post-treatment A	53.9 ± 0.3
19	Example 10	PGMA	Post-treatment A	65.7 ± 0.4
20	Example 10	PGMA	Post-treatment A	65.1 ± 0.3
21	Example 10	PGMA	Post-treatment A	65.0 ± 0.2
22	Example 11	PMMA	Post-treatment A	60.6 ± 0.6
23	Example 11	PMMA	Post-treatment A	59.2 ± 0.8
24	Example 11	PMMA	Post-treatment A	61.7 ± 1.2

Deposition of PMMA polymer from a solution by doctor blading.

A solution of PMMA polymer in anisole (10 wt%) was prepared by dissolving 2.76 g PMMA (996 kDa) in 25 mL anisole by mixing PMMA and anisole, sonicating for 30 minutes and stirring for 24h.

The PMMA polymer solution was doctor bladed onto the substrates listed in Table 3, with the methodology laid out in Example 3, using Post-treatment A.

The crosshatch testing was carried out as described in Example 5, according to the ASTM standard procedure described in Example 5. Finally, the adhesion of PMMA polymer on the different substrates was scored according to the ASTM standard described in Example 5. The scores are compiled in Table 4.

Fig. 20, upper left image, shows an image of the crosshatch testing on the blank Si substrate with doctor bladed PMMA polymer solution. From the large areas with loss of contact between the blank Si substrate and the PMMA polymer as well as apparent failure in adhesion between the blank Si substrate and PMMA polymer, and the ragged and frayed edges of the PMMA polymer

in the crosshatch cuts, it was concluded that adhesion was poor, supported by a set of ASTM scores across the three tested substrates of: 2B, 1B, 1B.

Fig. 20, upper middle image, shows an image of the crosshatch testing on the Si substrate modified with CPTMS and doctor bladed PMMA polymer solution. From the complete loss of contact between the Si substrate and the PMMA polymer indicating complete failure in adhesion between the Si substrate and PMMA polymer, it was concluded that adhesion was very poor, also indicated by a set of ASTM scores across the three tested samples of 0B, 0B, 0B.

Fig. 20, upper right, shows an image of the crosshatch testing of the Si substrate modified with PMAA surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, upper right image, the adhesion was quite poor, as the crosshatches generally presented with frayed and jagged edges and loss of some PMMA polymer material from said edges and crosses. The ASTM score across three substrates was 3B, 1B, 2B, supporting the notion of quite poor and varying adhesion between PMMA polymer and PMAA surface polymer.

Fig. 20 shows an image of the crosshatch testing of the Si substrate modified with PHEMA surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, middle left image, the adhesion was quite poor, indicated by the many frayed and jagged edges where the PMMA polymer has flaked off during the crosshatch cutting. This is supported by the ASTM score of 1B, 2B, 1B, across the three tested substrates.

Fig. 20, middle image, shows an image of the crosshatch testing of the Si substrate modified with PAAm surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, middle image, the adhesion was of rather poor quality, as a few of the crosshatches presented with straight edges, while most were quite frayed and jagged. This intermediate fairly poor between PMMA polymer and PAAm surface polymer is supported by an ASTM score of 2B, 2B, 2B, across the three tested substrates.

Fig. 20, middle right image, shows an image of the crosshatch testing of the Si substrate modified with PAMA surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, middle right image, the adhesion was very good as the crosshatches were intact and very sharply defined. Almost all edges are straight and defect free, with only a minority of edges

and crosses exhibiting a very low degree of flaking. These observations are supported by an ASTM score of 4B, 5B, 5B, across the three tested substrates.

Fig. 20, lower left image, shows an image of the crosshatch testing of the Si substrate modified with PGMA surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, lower left image, the adhesion was quite good as the crosshatches were mostly intact and only intermittent flaking was observed. This is supported by an ASTM score of 4B, 4B, 3B, across the three tested substrates.

Fig. 20, lower middle image, shows an image of the crosshatch testing of the Si substrate modified with PMMA surface polymer and doctor bladed with PMMA polymer solution. As can be seen from Fig. 20, lower middle image, no flaking was observed and no PMMA polymer was lost from the surface during the crosshatch testing. This indicates that the adhesion was exceptionally good as the crosshatches were intact and very sharply defined both in the crosses and along the cut lines. This is supported by an ASTM score of 5B, 5B, 5B, across the three tested substrates.

The results of the crosshatch test are summarized in Table 4 below along with the ASTM scores for the adhesion of PMMA polymer to the surface polymer.

Table 4. Summary of crosshatch tests.

Substrate material	**Surface modification**	**Description of crosshatch result**	**Score**
Si	None	Severe chipping and flaking of the PMMA squares.	2B, 1B, 1B
Si	CPTMS	No PMMA squares remained in the test grid area.	0B, 0B, 0B
Si	PMAA	All the PMMA squares are retained in the test grid area, with significant chipping of the test grid corners and lines.	3B, 1B, 2B
Si	PHEMA	All the PMMA squares are retained in the test grid area, with very severe chipping of the test grid corners and lines.	1B, 2B, 1B

Si	PAAm	All the PMMA squares are retained in the test grid area, with significant chipping of the test grid corners and lines.	2B, 2B, 2B
Si	PAMA	All PMMA squares remained in the test grid area and only very slight flaking and chipping was observed along test grid lines and corners.	4B, 5B, 5B
Si	PGMA	All the PMMA squares remained in the test grid area, with only slight chipping of the test grid corners and lines.	4B, 4B, 3B
Si	PMMA	All PMMA squares remained in the test grid area and no flaking and chipping was observed.	5B, 5B, 5B

Notably, the inventors have found that when it comes to promoting adhesion to PMMA polymer, any surface polymer with hydrogen bond donors (i.e. an electronegative atom such as N or O, bonded to a hydrogen atom) are relatively worse at promoting adhesion to PMMA polymer when compared to surface polymers that do not contain hydrogen bond donors. Namely the surface polymers with hydrogen bond donors in this example include PMAA (carboxylic acid, COOH functional group, ASTM score of 3B, 1B, 2B), PHEMA (hydroxyl group, OH functional group, ASTM score of 1B, 2B, 1B), and PAAm (amide, NH functional group, ASTM score of 2B, 2B, 2B) all have poor crosshatch scores for adhesion to PMMA polymer. Compare this to the surface polymers in this example that do not contain hydrogen bond donor moieties, namely PAMA (ASTM score of 4B, 5B, 5B), PGMA (ASTM score of 4B, 4B, 3B), and PMMA (ASTM score of 5B, 5B, 5B). This difference between surface polymers with hydrogen bond donors and surface polymers without hydrogen bond donors can likely be ascribed to the fact that the hydrogen bond donor-containing surface polymers tend to hydrogen bond with itself through intra-molecular interactions (all those polymers contain one or more hydrogen bond acceptors, such as the carbonyl oxygen atom, the ester oxygen atom, or the amide nitrogen atom), rather than interact strongly with the PMMA surface polymer through intermolecular interactions. Furthermore, the inventors anticipate poor or no mixing between the hydrogen bond donor-containing polymers and PMMA, meaning that physical entanglement of the surface polymer and the PMMA polymer cannot contribute significantly to the adhesion. Conversely, the surface polymers that do not contain

hydrogen bond donor moieties are comparatively less polar than the hydrogen bond donor moiety-containing surface polymers. These surface polymers can be expected to mix more with the PMMA polymer, leading to adhesion through both Van der Waals interactions as well as through physical entanglement of the surface polymer and the PMMA polymer. This effect is expected to be the strongest between PMMA surface polymer and PMMA polymer, which is supported by the highest ASTM crosshatch score of 5B across all three substrates with PMMA surface polymer that was tested in this example.

Example 14

Coating of poly(imide) (PI) on surface polymer-modified substrates.

This example demonstrates how certain surface polymers promote adhesion to PI polymers which are doctor bladed onto the substrates as a solution of poly(amic acid), specifically poly(pyromellitic dianhydride-co-4,4′-oxydianiline), which is subsequently converted to poly(imide) through a heating step, wherein a condensation converts the poly(amic acid) to poly(imide). The inventors discovered a correlation between the polarity and structure of the surface polymers and the obtained adhesion, indicated by crosshatch testing according to the ASTM standard scoring system.

A variety of surface polymers were prepared as indicated in Table 5, and adhesion to PI polymer was tested for each surface polymer type. Substrate 1 in Table 5 is not modified with surface polymers and serves as a reference sample and will be referred to as a blank substrate. This blank substrate was cleaned by sonicating in iPrOH for 10 minutes and air dried prior to doctor blading the solubilized poly(amic acid) solution. Substrates 2 to 8 were all pre-treated as described in Example 1, using Substrate Preparation Procedure A, and had polymerization initiator (CPTMS) deposited as described in Example 2, CPTMS Procedure A.

Table 5. Average dry film thicknesses as determined by ellipsometry.

Substrate no.	**Surface polymer preparation Example No.**	**Surface Polymer Type**	**Doctor Blading post-treatment (Example 3)**	**Surface Polymer Thickness**
1	Not relevant	No surface polymer, blank	Post-treatment A	Not relevant
4	Not relevant	No surface polymer, CPTMS only	Post-treatment A	Not relevant
7	Example 6	PMAA	Post-treatment A	35 ± 1
10	Example 7	PHEMA	Post-treatment A	58 ± 2
13	Example 8	PAAm	Post-treatment A	10 ± 1
16	Example 9	PAMA	Post-treatment A	43 ± 1
19	Example 10	PGMA	Post-treatment A	49 ± 1
22	Example 11	PMMA	Post-treatment A	72 ± 1

The substrates listed in Table 5 were coated with a solution of a poly(amic acid), specifically poly(pyromellitic dianhydride-co-4,4′-oxydianiline convertible to polyimide (PI), by doctor blading as described in Example 3 and subjected to post-treatment B as described in Example 3. The heating during post-treatment B converts the poly(amic) acid into the PI structure through condensation of the amide and the carboxylic acid of the poly(amic acid) structure.

Evaluation of adhesion promotion between substrate and PI polymer by crosshatch testing

The poly(imide) coated substrates were crosshatch tested in accordance with Example 5, using the ASTM standard and scored according to Fig. 24. The crosshatch results can be seen in Fig. 21, and the crosshatch results are summarized in Table 6 below.

Table 6. Crosshatch testing results of 8 substrates with PI polymer (doctor bladed and post-baked (according to Example 3, Post-treatment B)). "Surface modification" refers to surface polymer propagated from polymerization initiator CPTMS. Crosshatches were scored according to ASTM.

Substrate material	**Surface modification**	**Description of crosshatch result**	**Score**
Si	None	No PI squares retained in the tested area	0B
Si	CPTMS	No PI squares remained in the tested area.	0B
Si	PHEMA	All PI squares remained in the test grid area with no chipping of the test grid corners.	5B
Si	PAAm	All the PI squares are retained in the test grid area, with chipping of the test grid corners.	4B
Si	PAMA	No PI squares remained in the test grid area.	0B
Si	PGMA	All the PI squares remained in the test grid area, with slight chipping of grid corners.	4B
Si	PMAA	3 PI squares lost from the tested area, slight chipping of grid corners and edges.	3B
Si	PMMA	No PI squares retained in the test area.	0B

Based on the results summarized in Table 6 above, some inferences can be made as to which types of surface polymers are well suited for bonding PI polymer. Firstly, consider that PI polymer contains several hydrogen bond acceptors (O and N atoms not bonded to hydrogen). This led the inventors to expect strong interactions between PI and the surface polymers that contain hydrogen bond donors such as OH and NH moieties. In line with this, the surface polymers of PHEMA (ASTM score of 5B) and PAAm (ASTM score of 4B) both bonded very well or excellent to PI, as well as the PMAA surface polymer (ASTM score of 3B) bonded somewhat to PI. These surface polymers comprise hydrogen bond donors by virtue of the O-H functional group (PHEMA and PMAA) or the N-H functional group of PAAm. Surprisingly, the PGMA surface polymer also bonded very well to PI but does not initially comprise a hydrogen bond donor moiety. The heating during the post-baking-treatment of the deposited poly(amic acid) polymer can be expected to lead to hydroxyl group formation on the PGMA surface polymer by virtue of the ring opening reaction of the epoxy functional group of PGMA surface polymer through thermal activation or the reaction with the water released from the PI-forming condensation reaction of the poly(amic acid) polymer during post-baking. Thus, this surface polymer is expected to contain hydroxyl groups at the time

of crosshatch testing, providing an explanation for the strong adhesion within the framework of hydrogen bond donors on the surface polymer leading to strong adhesion to the PI polymer. Conversely, the inventors anticipated lower interaction, i.e., worse adhesion, between PI polymer and the surface polymers that do not contain hydrogen bond donor moieties. In line with this, the PMMA surface polymer, PAMA surface polymer, and CPTMS polymerization initiator modifications all failed to bond PI in this experiment. These 3 modifications do not comprise hydrogen bond donors, i.e., comprising no functional groups containing a hydrogen atom bonded to a strongly electronegative atom such as O-H and N-H, and thus cannot be expected to interact strongly with the PI polymer that contains only hydrogen bond acceptors (N and O atoms not bonded to H atoms).

Example 15

Adhesion of spincoated PMMA to PMMA surface polymer modified substrates.

This example demonstrates spin coating of a thin film of PMMA polymer onto Si and Si with PMMA surface polymer substrates, as well as the crosshatch evaluation of the adhesion of such substrates.

A 2 wt% solution of PMMA (996 kDa) was prepared in anisole by dissolving 1999.6 mg PMMA in anisole (96.5 mL) by stirring overnight.

The solution of 2 wt% PMMA in anisole was spin coated onto blank Si wafers, pre-cleaned by sonication in IPA for 5 minutes and on Si substrates which were pre-treated as described in Example 1, Substrate Preparation C, and with CPTMS deposited as described in Example 2, CPTMS Procedure B. The spin coating was performed as described in Example 4, using a final spin speed of 1000 RPM. The thickness of the PMMA surface polymer and the thickness of the spin coated PMMA polymer is reported in Table 7.

Table 7. Thickness of substrate with surface polymer, substrate with surface polymer and spincoated PMMA polymer, and blank substrate with spincoated PMMA polymer. Thicknesses were determined by ellipsometry (as average dry film thickness).

Substrate ID	Surface polymer thickness [nm]	PMMA polymer (spincoat + surface polymer) thickness [nm]
Blank Si-1	-	79.5 ± 19.2
Si-PMMA-1	59.3 ± 0.6	140.5 ± 20.3

The spin coated film thickness exhibits comparatively higher standard deviation than that of the surface polymer, and this is caused by the substrate geometry leading to striations and a thicker spin coated film in the center of the substrate. The following crosshatch test was evaluated in the center of the substrates where the thickest and more homogeneously spin coated layer of PMMA polymer was obtained.

The adhesion of the PMMA polymer to the substrates was evaluated as described in Example 5, using the ASTM standardized method and scoring. The results are shown in Fig. 22 and Fig. 23. Quite surprisingly, no PMMA squares were peeled from either substrate type (Blank Si (Fig. 22 B)) and Si with PMMA surface polymer (Fig. 22 A)), and at first look the PMMA cuts appeared similar between blank Si and PMMA surface polymer substrates. The inventors speculate that the adhesion between PMMA surface polymer and PMMA polymer is stronger than that of blank Si and PMMA polymer and believe that the lack of a clear difference between on the one hand PMMA surface polymer and PMMA polymer, and on the other hand blank Si and PMMA polymer may be due to the tape used for peeling adhering too weakly for this type of polymer. Thus, a more strongly adhering tape could be expected to lead to a clearer differentiation of adhesion. However, slight details in the quality of the cuts (see Fig. 23, zoomed photos of the marked dark squares in Fig. 22, where Fig. 23 A) is Si substrate with PMMA surface polymers and spincoated PMMA polymer, and Fig. 23 B) is blank Si substrate with spincoated PMMA polymer) made during the crosshatch test reveal that the substrate with PMMA surface polymer promotes straighter edges and cleaner cuts than observed in case of the blank Si substrate. Such subtle details may be of tremendous importance in certain applications, such as the bonding and patterning of photoresists in the semiconductor field. Here, tiny variations in quality and smoothness of the photoresist may

lead to fatal flaws in downstream processing steps. Thus, the inventors envision the use of surface polymers to improve the quality of photoresist layers that are applied through e.g. spin coating.

List of reference numerals

100	Substrate decorated with surface polymers
110	Tape
120	Substrate decorated with surface polymers and polymer doctor bladed onto the substrate
130	Substrate
140	Surface polymer attached to substrate
170	Polymer adhered to substrate through surface polymers
200	Substrate decorated with surface polymers and polymer doctor bladed onto the substrate
210	Crosshatches
230	Tape for crosshatch testing
240	Crosshatches remaining on substrate after peeling of tape for crosshatch testing
250	Peeled-off crosshatches
260	Peeled-off crosshatches
1901	Negative electrode current collector
1902	Negative electrode active material
1903	Surface polymer
1904	Separator, electrolyte
1905	Surface polymer
1906	Positive electrode active material
1907	Surface polymer
1908	Positive electrode current collector
2502	Polymerization initiator-modified substrate
2503	Substrate displacement device
2504	Reaction composition container
2505	Reaction composition
2506	Polymerization initiator chemistry container
2507	Polymerization initiator chemistry
2509	Annealing oven
2511	Annealing oven gas environment
2514	Cleaning container
2516	Cleaning agent/device
2604	Recation composition container
2610	Reaction composition

2618 Roll-to-roll processor

2620 Rollers

2621 Sending roll

2622 Receiving roll

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CLAIMS

1. A method of adhering a polymer to a surface of a substrate comprising:

providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate,

exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate , and

depositing a polymer on the at least one surface of the substrate,

to provide an adhering interface between the surface polymer and the polymer.

2. A method according to claim 1, where the deposited polymer is a thin film of polymer material.

3. A method according to claim 1, wherein the polymer is solubilized in a solvent.

4. A method according to claim 1, wherein the surface polymer comprises one or more functional groups compatible with one or more functional groups in the polymer.

5. A method according to claim 4 wherein the one or more functional groups of surface polymer are selected from hydroxyl groups, amine groups, and amide groups.

6. A method according to claim 4, wherein the one or more functional groups of the polymer are methyl ester groups.

7. A method according to claim 1, wherein the monomer is comprised in a reaction composition comprising:

a catalyst,

a ligand,

an activator, and

a solvent.

8. A method according to claim 7, wherein the catalyst is obtained from copper (Cu), iron (Fe) or ruthenium (Ru).

9. A method according to claim 7, wherein the ligand is selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), and/or 2,2'-bipyridyl (BiPy).

10. A method according to claim 7, wherein the activator is selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose, glucose with glycose oxidizing enzyme (GO_x), and/or pyrogallic acid.

11. A method according to any one of claims 1-10, wherein the solvent is an aqueous solvent.

12. A method according to any one of claims 1-10, wherein the reaction composition further comprises a buffer.

13. A method according to any one of claims 1-10, wherein the reaction composition further comprises a halogen salt.

14. A method according to any one of claims 1-10, wherein the reaction composition further comprises a surfactant.

15. A method according to any one of claims 1-10, wherein the reaction composition further comprises a polyquaternium compound.

16. A method according to any one of claims 1-15, wherein the surface polymer comprises poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(methacrylate) (PMAA), poly(methyl methacrylate) (PMMA), poly(glycidyl methacrylate) (PGMA), poly(allyl methacrylate) (PAMA).

17. A method according to any one of claims 1-15, wherein the polymer is poly(acrylic acid) (PAA), poly(amic acid), and poly(methyl methacrylate) (PMMA).

18. A method according to any one of claims 1-15, wherein the surface polymer is poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), or poly(glycidyl methacrylate) (PGMA), and the polymer is poly(methyl methacrylate) (PMMA), or poly(amic acid).

19. A method according to claim 1, wherein the interface is dried, UV cured, or post-baked following deposition of the polymer.

20. A method according to claim 1, wherein the substrate comprises silicon, copper, glass, ceramic and/or steel.

21. A method according to claim 1, wherein the polymer is deposited by doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

22. A device stack comprising

a substrate with a first surface,

a surface polymer on at least a portion of a first surface covalently attached to the substrate via polymerization initiators covalently attached to the substrate, and

a deposited polymer covering and adhering to at least a portion of the surface polymer.

23. A device according to claim 22, wherein the deposited polymer forms a thin film on the substrate.

24. A device according to claim 23, wherein the thin film has a thickness in the range 1 nm to 30 μm.

25. A device stack according to claim 22 or 23, wherein the substrate comprises silicon, copper, glass, ceramic and/or steel.

26. A device stack according to claim 22, wherein the polymer is deposited by doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

27. A device stack according to any one of claims 22-26, wherein the surface polymer comprises poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylamide) (PAAm), or poly(glycidyl methacrylate) (PGMA), and the polymer is poly(methyl methacrylate) (PMMA), or poly(amic acid).

28. A device stack according to any one of claims 22-26, wherein the polymer is poly(acrylic acid) (PAA), poly(amic acid), and poly(methyl methacrylate) (PMMA).

28. A device stack according to any one of claims 22-26, wherein the surface polymer is poly(methyl methacrylate) (PMMA), and the polymer is poly(methyl methacrylate) (PMMA).

29. A device stack comprising

a substrate with a first surface,

a surface polymer on at least a portion of a first surface covalently attached to the substrate via polymerization initiators covalently attached to the substrate, and

a deposited polymer covering and adhering to at least a portion of the surface polymer, wherein the surface polymer is formed by

providing a substrate having polymerization initiators covalently bound to at least a portion of a surface of the substrate,

exposing the substrate to a reaction composition comprising a monomer to form surface polymers covalently bound to the polymerization initiators on the substrate.

30. A device stack according to claim 29, wherein the reaction composition further comprises

a catalyst,

a ligand,

an activator, and

a solvent.

31. A device stack according to claim 30, wherein the catalyst comprises copper (Cu), iron (Fe) or ruthenium (Ru).

32. A device stack according to claim 30, wherein the ligand is selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), and/or 2,2`-bipyridyl (BiPy).

33. A device stack according to claim 30, wherein the activator is selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose, glucose with oxidizing enzyme (GO_x), and/or pyrogallic acid.

34. A device stack according to claim 30, wherein the solvent is an aqueous solvent.

35. A device stack according to claim 30, wherein the reaction composition further comprises a buffer.

36. A device stack according to claim 30, wherein the reaction composition further comprises a halogen salt.

37. A device stack according to claim 30, wherein the reaction composition further comprises a surfactant.

38. A device stack according to claim 30, wherein the reaction composition further comprises a polyquaternium compound.

39. A device according to claim 29, wherein the polymer is deposited by doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

40. A method of preparing a device stack according to any one of claims 22-39 comprising

providing the substrate, wherein surface polymers are present on at least a portion of the surface of the substrate,

providing a polymer, and

depositing the polymer on the surface of the substrate to provide an adhering interface between the surface polymer and the polymer.

41. A method according to claim 40, wherein the deposited polymer is a thin film of polymer material.

42. A method according to claim 40, wherein the polymer is provided solubilized in a solvent.

43. A method according to claim 40, wherein the polymer is deposited by doctor blading, spin coating, spray coating, dip coating, flow coating, physical vapor deposition, comma coating, or slot-die coating.

44. A method according to claim 40, further comprising, after the depositing, drying, UV curing, and/or post-baking the deposited polymer.

45. A method according to claim 40, wherein the substrate comprises silicon, copper, glass, ceramic and/or steel.

46. A system for forming a device stack according to any one of claims 22-39, the system comprising:

a reaction composition container containing a reaction composition, said reaction composition comprising:

a monomer,

a catalyst,

a ligand,

a catalyst activator, and

a solvent,

a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time,

wherein the controlled time is sufficient for surface polymers to be formed on the portion of the polymerization initiator-modified substrate,

a polymer deposition system for depositing a polymer at least over a portion of the formed surface polymer,

wherein the substrate displacement device is further configured for bringing the surface polymer coated substrate into the polymer deposition system for a controlled time, and wherein the controlled time is sufficient for depositing a polymer on at least a portion of the surface polymers, and optionally

a device for drying, curing, or post-baking the polymer following the depositing of the polymer.

47. A system according to claim 46, wherein the substrate displacement device comprises any one of:

a conveyor system,

a programmable mechanical arm, or

a roll-to-roll mechanism.

48. A system according to claim 46 or 47, further comprising a polymerization initiator container containing a polymerization initiator agent, wherein the substrate displacement device is further configured to bring the portion of the substrate for attachment of polymerization initiators into contact with the polymerization initiator agent to form polymerization initiators at the substrate surface, prior to bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition.

49. A system of any one of claims 46-48 further comprising a cleaning container, the cleaning container containing a cleaning agent, wherein the substrate displacement device is configured to bring the portion of the polymerization initiator-modified substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition, and optionally

the substrate displacement device is configured to bring the portion of substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator.

50. A system of claim 49, wherein the polymerization initiator container is a vacuum oven.

51. A system according to claim 46, wherein the polymer deposition system comprises a doctor blade coater configured to spread the polymer on to the surface polymer, a spin coater configured to spin coat the polymer on to the surface polymer, a comma coater configured to spread the polymer on to the surface polymer, or a slot-die coater configured to spread the polymer on to the surface polymer, a spray coater for spraying the polymer in a volatile carrier solvent on to the surface polymer, a dip coating tank for applying the polymer on to the surface polymer, a flow coating tool for gravity flowing the polymer in a volatile carrier solvent over the surface polymer, or a vacuum chamber configured for physical vapor deposition of the polymer on to the surface polymer.