

**COMPOSITIONS OF MATTER, RESIST STRUCTURES INCLUDING A
LAYER OF ELECTRICALLY CONDUCTIVE POLYMER HAVING
CONTROLLED pH AND METHODS OF FABRICATION THEREOF**



FIELD OF THE INVENTION

The present invention is directed to electrically conductive compositions of matter having controlled pH, structures fabricated therewith having a layer of energy sensitive material and a layer of electrically conductive polymer having a controlled pH and methods of fabrication thereof. More particularly the structures according to the present invention are useful in fabricating electronic devices wherein the energy sensitive material is a resist.

BACKGROUND OF THE INVENTION

In many industrial applications a pattern is created in a layer at the surface of a fabricated object. In particular, in microelectronics the various intricate patterns necessary to form, for example, the various doped regions of silicon on a chip or their interconnections or the various interconnections on a package are delineated by lithographic techniques. Lithography relies on energy sensitive materials generally called resists. An energy sensitive material is disposed on a surface. The layer of energy sensitive material is exposed to a pattern of energy which alters the properties of the

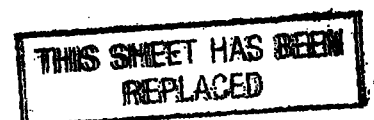
layer in the exposed regions so that either the exposed or unexposed regions can be subsequently removed to form a pattern in the energy sensitive layer. In positive acting resists the exposed regions become soluble whereas in negative acting resists the exposed regions become insoluble. In either case a pattern has been generated in the resist or energy sensitive layer. This pattern can then be transferred down to underlying layers by various etching mechanisms.

Where the pattern of energy results in generation of electrical charge or carries an electrical charge, electrical charge can in turn accumulate at the energy sensitive layer or in the underlying layers which can result in distortion of the pattern being created in the energy sensitive layer. Such distortions create huge image placement variations and errors. This occurs when a dielectric energy sensitive material such as a resist is exposed to a charged beam such as an electron beam or an ion beam. The dielectric energy sensitive layer accumulates charge from the beam. The accumulated charge introduces electric fields which after reaching a sufficient magnitude distorts the beam and results in a misplacement of the beam on the energy sensitive material. This creates errors in the pattern being formed in the layer.

This can be avoided by disposing on, under or within the energy sensitive layer a layer of electrically conductive material which can be used to drain off the accumulated charge and remove or reduce the undesired electric field.

Electrically conductive organic polymers are a class of electronic materials that combine the electrical properties of metals with the processability and mechanical properties characteristic of metals. Examples of such polymers include polyparaphenylene vinylenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfuranes,

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polypyrroles, polyselenophenes, poly-p-phenylene sulfides, polythianaphenes, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

These polymers are conjugated systems which are made electrically conducting by doping. The non-doped or non-conducting form of the polymer is referred to herein as the precursor to the electrically conducting polymer. The doped or conducting form of the polymer is referred to herein as the conducting polymer.

Conducting polymers can be utilized as thin charge dissipative coatings to prevent charging in the application described above. In addition, they have potential for a large number of other applications in such areas as electrostatic charge/discharge (ESC/ESD) protection, electromagnetic interference (EMI) shielding, resists, electroplating, corrosion protection of metals and ultimately metal replacements, i.e. wiring, plastic microcircuits, conducting pastes for various interconnection technologies (solder alternative) etc..

The polyaniline class of conducting polymers has been shown to be one of the most promising and most suited conducting polymers for a broad range of commercial applications. The polymer has excellent environmental stability and offers a simple, one-step synthesis. A number of soluble derivatives can be made. For example, we previously disclosed a new family of water soluble conducting polyanilines in U.S. patent 5,370,825, the teaching of which is incorporated herein by reference. These water based polymers are ideally suited as spin applied charge dissipative layers. One problem with these polymers as well as most of the doped polyanilines is that the doped polymer is acidic, i.e. has low pH. The acidic nature of these polymers poses a concern in many applications. For example, if the polyaniline is used as a charge dissipative coating on

top of a resist, the acid functionality can contaminate the resist as most current resists are extremely sensitive to acid. In addition, in other applications where the conducting polymer is applied on to a plastic or a metal, the acid can pose significant problems such as induce degradation, corrosion, and so fourth.

It is therefore desirable to be able to control the pH of the doped conducting polymer and to do so without impacting the conductivity. Herein conducting polymer compositions with controlled pH and methods of fabricating such polymers are described.

OBJECTS

It is an object of the present invention to provide an electrically conductive polymer having controlled pH.

It is an object of the present invention to provide a method of forming an electrically conductive polymer having controlled pH.

It is an object of the present invention to provide a method of forming an electrically conductive polymer having controlled pH bu including acid neutralizing functionality with the conductive polymer. e.

It is an object of the present invention to provide a method of forming an electrically conductive polymer having controlled ph by treating said acidic conductive polymer with a suitable base to neutralize the acid functionality to a controlled degré.

It is an object of the present invention to provide a structure having a surface containing an electrically conducting polymer having controlled pH.

It is another object of the present invention to provide structures having patterns of electrically onductive polymers on a surface.

SUMMARY OF THE INVENTION

A broad aspect of the present invention is an electrically conductive composition of matter having a controlled pH.

Another broad aspect of the present invention is a structure having a surface having thereon an electrically conductive polymer having a controlled pH.

A more particular aspect of the present invention is a structure having a surface having a pattern thereon of on electrically conductive polymer having a controlled pH.

Another broad aspect of the present invention is a structure having: a surface; a plurality of layers on the surface; at least one of the plurality of layers is formed from an energy sensitive material; at least another layer is formed from an electrically conductive polymer; the electrically conductive polymer contains acid functionality; and the electrically conductive polymer has a predetermined pH.

Another broad aspect of the present invention is a method of disposing on a surface an electrically conductive polymer having a controlled pH.

Another more particular aspect of the present invention is a method of disposing on a surface a plurality of layers; at least one of the plurality of layers is formed from an energy sensitive material; at least another layer is formed from an electrically conductive polymer; the electrically conductive polymer contains acid functionality; and the electrically conductive polymer has a predetermined pH.

BRIEF DESCRIPTION OF THE DRAWINGS

Further objects, features, and advantages of the present invention will become apparent from a consideration of the following detailed description of the invention when read in conjunction with the drawing FIGs., in which:

Fig. 1 is a general formula for a polyaniline; (a) is the precursor form of the polymer or the non-doped form of the polymer; (b) is the doped form of the polymer or the electrically conducting form of polyaniline; (c) is the actual structure for the doped electrically conducting polymer consisting of a polysemiquinone radical cation.

Fig. 2 depicts the structure of the water soluble polyacid/polyaniline material.

Fig. 3 depicts electrically conducting polyaniline having excess acid functionality.

Fig. 4 depicts .25 μ m features delineated with UV3 containing polyaniline with a pH of 1.9 on top. The polyaniline was left in place during the resist post exposure bake. As can be seen, severe thinning is observed due to acid contamination from the polyaniline into the resist.

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Figs. 5a, 5b 5c and 5d (for polyaniline, pH = 1.9, pH = 2.5 and pH = 5.0, respectively) depict .15um features with polyaniline of various pHs on UV3 resist. The polyaniline is removed before the PEB in all cases. Lithography of the resist looks good, indicating that there is no contamination issues.

Fig. 6 depicts polyaniline with pH of 1.9 on UV3. The polyaniline is post apply baked at 80 C for 5 minutes. There is no effect on resist lithography is observed due to the polyaniline bake.

Fig. 7 depicts polyaniline with pH of 2.5 on UV3. The polyaniline is post apply baked at 80 C for 5 minutes. There is no effect on resist lithography is observed due to the polyaniline bake.

Fig. 8 depicts the shelf life of UV3 with and without polyaniline top coat. As can be seen, the polyaniline extends the shelf life of the polymer to 24 days at which time the experiment was stopped.

DETAILED DESCRIPTION

The present invention is directed to electrically conducting polymers having controlled pH and to structures fabricated therewith. Examples of such polymers that can be used to practice the present invention are of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and copolymers of monomers thereof. The general formula for these polymers can be found

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in U.S. Patent 5,198,153 to Angelopoulos et al. the teaching of which is incorporated herein by reference. The present invention will be described with reference to one type of polymer which is a substituted or unsubstituted polyaniline or copolymers of polyaniline having general formula shown in Fig. 1 wherein each R can be H or any organic or inorganic radical; each R can be the same or different; wherein each R¹ can be H or any organic or inorganic radical, each R¹ can be the same or different; $x \geq 1$; preferably $x \geq 2$ and y has a value from 0 to 1. Examples of organic radicals are alkyl or aryl radicals. Examples of inorganic radicals are Si and Ge. This list is exemplary only and not limiting.

The precursor to the electrically conducting polymer form is shown in Fig. 1a. This is the non-doped form of the polymer or the base polymer. Fig. 1b shows polyaniline doped with a dopant. If the polyaniline base is exposed to cationic species QA, the nitrogen atoms of the imine part of the polymer becomes substituted with the Q⁺ cation to form an emeraldine salt as shown in Fig. 1b. Q⁺ can be selected from H⁺ and organic or inorganic cations, for example, an alkyl group or a metal.

QA can be a protic acid where Q is hydrogen. When a protic acid HA is used to dope the polyaniline, the nitrogen atoms of the imine part of the polyaniline are protonated. The emeraldine base form is greatly stabilized by resonance effects. The charges distribute through the nitrogen atoms and aromatic rings making the imine and amine nitrogens indistinguishable. The actual structure of the doped form is a delocalized polysemiquinone radical cation as shown in Fig. 1c.

Polyaniline can exist in a number of oxidation states. The emeraldine form of the polymer refers to the material that consists of approximately equal number of benzenoid

units and quinoid units ($y \approx .5$ in Fig. 1). The emeraldine polymer can be reduced to the leucoemeraldine polymer where $y=1$ in Fig. 1. The leucoemeraldine base form of the polymer is not stable in ambient conditions. The emeraldine polymer can be oxidized to the pernigraniline form where $y=0$; however, the fully oxidized form of the polymer also tends not to be stable. In principle, other oxidation states intermediate between $y=0$ and $y=1$ are possible. The emeraldine base form of the polyaniline is the most stable form. Because of its environmental stability, it is the form of polyaniline that has been the most abundantly studied and is the form that is suited for technological applications. The most preferred embodiment of the present invention is emeraldine base form of the polyaniline wherein y has a value of approximately 0.5.

As can be seen from Fig. 1c, the doped polyaniline is acidic because it is generally doped with a protonic acid. The dopant can consist of single molecules, oligomers and polymers. For example, previously we described a series of water soluble polyanilines that were made by polymerizing aniline in the presence of a polyacid which are described in U.S. patent 5,370,825, the teaching of which is incorporated herein by reference. As the polyaniline forms during the polymerization reaction, it wraps around the polyacid resulting in a blend of the polyaniline/polyacid (Figure 2). Examples of polyacids are polystyrenesulfonic acid, polyacrylamidopropane sulfonic acid, and so fourth as described in (PATENT #). In the final conducting polyaniline/polyacid blend, the polyacid has functional sulfonic acid groups which are not used to dope the polyaniline. Thus, there are free sulfonic acid groups rendering the polyaniline quite acidic. The number of free sulfonic acid groups determines the acidity or pH of the polymer. As made, the polymer can be very acidic, $\text{pH} = 1$ to 1.5.

Figure 3 depicts a general view of a doped polyaniline having excess acid functionality. This acid can be on the polyaniline backbone and/or on the counteranion of the dopant molecule. This excess acid poses significant concerns when the polyaniline is applied on to resists or acid sensitive plastics or metals. For example, in applying polyaniline on top of resists to prevent charging during electron beam irradiation or SEM metrology, the acid functionality of the polyaniline contaminates the resist.

Most resists in the industry are chemically amplified (CA) consisting of a photoacid generator (PAG) and a polymer containing acid sensitive deblockable groups. Upon irradiation, the PAG forms an acid. This acid begins to deblock the acid sensitive functional groups on the polymer. The key to the high performance of the CA resists is that only a catalytic amount of acid is necessary to start a very efficient deprotection reaction. The reason for this is that the acid which is formed upon irradiation is only a catalyst. As it begins to deprotect the acid sensitive functional groups, additional acid is released from the deprotection mechanism which then acts as a catalyst for subsequent deprotection. Thus, one proton begins a cascade of reactions which are self catalyzed. Because of this mechanism, CA resists are very efficient and have very high sensitivity. At the same time, because of this sensitivity to acid, they are easily contaminated by any traces of acid thereby destroying the excellent lithographic performance of the resist. It is key therefore to be able to control the pH of any material that is applied on/in/or below CA resists. CA resists are also sensitive to temperature since acid diffusion can occur rendering unexposed regions exposed to acid. Temperature coupled with free acid can destroy the lithographic performance of CA resists.

Acid in general can catalyze metal corrosion, degradation of plastics and so fourth. It is therefore desirable to be able to control the final pH of a conducting polymer to prevent these problems.

In order to control the pH of the polyaniline materials, the acidic polyaniline is treated with a neutralizing agent, such as a suitable base, to neutralize some or all of the acid groups. The base is added to the polyaniline in a quantity suitable to adjust the pH from 0 to 14, preferably from 1 to 7 and most preferably from 1 to 5.

A list of suitable bases include: tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride, and so fourth. This list is exemplary only and not limiting.

EXAMPLES:

The unsubstituted polyaniline in the emeraldine form is synthesized by the chemical oxidative polymerization of aniline in 1N HCl using ammonium peroxydisulfate as an oxidizer. Polyaniline can also be oxidatively polymerized electrochemically as taught by W. Huang, B. Humphrey, and A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 1, 82, 2385, 1986. In the chemical synthesis, the conducting polyaniline hydrochloride (emeraldine hydrochloride) salt precipitates from solution. The polymerization is allowed to proceed for several hours after which the powder is filtered, washed with excess 1N hydrochloric acid. The emeraldine hydrochloride is then converted to the non-conducting or non-doped emeraldine base by reaction with 0.1M ammonium

hydroxide. The emeraldine base is then filtered, washed with ammonium hydroxide, then washed with methanol and dried. The polymer at this stage is in the undoped emeraldine base form as a powder.

Substituted (either on the aromatic ring or on the nitrogen) polyanilines in the emeraldine form are synthesized in the same fashion as above but using the appropriate substituted aniline monomer in the polymerization reaction. Copolymers are made by the oxidative polymerization of one or more monomers. Other acids can also be used in the polymerization reaction other than hydrochloric acid. Aqueous acetic acid, sulfuric acid, organic sulfonic acids, such as aqueous toluenesulfonic acid, dodecylbenzenesulfonic acid, camphorsulfonic acid, and so on. The o-ethoxy substituted polyaniline was prepared by oxidative polymerization of o-ethoxy aniline in 1N hydrochloric acid as described above. Copolymers having various amounts of o-ethoxy content were synthesized by polymerizing o-ethoxyaniline and aniline in aqueous 1N hydrochloric acid. The amount of o-ethoxy content in the final polymer was controlled by varying the feed ratio of this monomer in the initial polymerization reaction.

The substituted and unsubstituted emeraldine base powder is generally processed by dissolving the powder in an organic solvent. The unsubstituted emeraldine base was dissolved in NMP at a 5-10% concentration or DMPU. The solution can be used to spin-coat films of the emeraldine base polymer on silicon wafers, quartz wafers, salt plates, and so on. These films were on the order of 500 Å to 1.0 μm . Thicker films (on the order of 50 to 200 μm) were made by solution casting techniques in which the solution was poured into an aluminum pan or glass dish and placed into a vacuum oven at 60 C for 24 hours. The solution can also be used to process the material into a structural part or into a fiber. The substituted emeraldine base such as the o-ethoxy

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substituted emeraldine base was more soluble than the unsubstituted emeraldine base. This polymer can be dissolved in cyclohexanone, tetrahydrofuran, ethyl lactate and so on. A solution was made in cyclohexanone (5% solids) and this solution was used to process films (thin and thick).

The polyanilines in the nondoped form can be treated with a dopant such as hydrochloric acid, acetic acid, formic acid, polystyrenesulfonic acid, acrylamidopropanesulfonic acid, polyacrylic acid and so forth to render the material conducting.

The water soluble polyaniline was made as described in US patent 5,370,825, the teaching of which is incorporated herein by reference. The polymer as made has a pH of 1.9. The pH was increased to 2.0 to 2.5 to 3.0 and to 5.0 by addition of a base such as tetramethyl ammonium hydroxide. The polyaniline powder can be treated in the solid state with a solution of the base. The polyaniline can be dissolved and treated with the base in solution. The polyaniline can be made into a film or a structural part and treated with a solution of the base. Furthermore, the polyaniline can be treated during the synthesis as follows: When the polyaniline is isolated from the reaction mixture it can be washed with a solution of the base.

Examples will be given where polyaniline was used as a dissipative coating on top of a dielectric energy sensitive material both positive tone and negative tone resists.

Example 1: Polyaniline used on top of a positive tone resist, UV3

The energy sensitive photoresist used in this experiment was UV3, a commercial deep-UV photoresist made by IBM/Shipley. This material has well known and documented e-beam sensitivity. The resist was spin coated at 4850rpm to get a thickness of approximately 0.32um, and baked at 140°C for 3 minutes. The water soluble polyaniline was applied by spin coating on top of the baked UV3 photoresist. Since UV3 is a chemically amplified photoresist, contamination from basic airborne compounds or materials coated on top of the photoresist have the potential for impeding the imaging properties of the resist. To address this issue, electrically conductive coatings of different pH's were applied on top of UV3. Additional experiments were done to determine how processing conditions of the electrically conductive layer effect the imaging properties of the photoresist. In these experiments, baking the electrically conductive layer after spin coating (PAB), and the absence/presence of the electrically conductive top coat during the post exposure bake step (PEB) were examined. Exposures were done on a 25KeV e-beam tool.

The effect of the pH of the polyaniline on the lithographic properties of UV3 was examined by patterning UV3 wafers that had been coated with polyaniline of pH 1.9 and pH 5. In these experiments the polyaniline was not given a post apply bake. Since this bake is an additional process step, in a manufacturing environment this would translate into a more costly process. In one set of experiments, the polyaniline was rinsed off in water after the exposure but before the post exposure bake. In a second set of experiments, the polyaniline was left in place during the post exposure bake and was rinsed off immediately before development. Results of that experiment can be seen in table 1.

From these results it can be concluded that the processing and pH of polyaniline has a significant effect on the lithography of the resist. If the polyaniline is left in place during the PEB, the resist response is different depending on the pH of the material. For the low pH version, $\text{pH} = 1.9$, the resist thinned and the patterns were gone. This indicates that the acid functionality in the polyaniline are diffusing into the resist during the bake step, causing deblocking of the polymer and thinning of the resist. (See Figure 4). For the high pH material, $\text{pH} = 5$, the resist did not develop if the polyaniline was left in place during the PEB. This indicates that the base which was added to adjust the pH is contaminating the UV3 photoresist. The base is scavenging the acid causing no chemistry to occur in the resist. If the polyaniline is removed before the PEB, it appears to have no effect on the lithography of the resist. Excellent resolution and sensitivity is attained (see Figure 5).

Additional experiments were conducted to determine if baking the polyaniline after it is applied has any effect on the lithography. Tests were done using the 1.9 pH material and 2.5 pH material with a 5 minute bake at 80°C . The polyaniline was rinsed off before the PEB. Lithography was unchanged compared to the unbaked samples (Figures 6 & 7).

Using the low pH material and rinsing before PEB, shelf life tests were conducted on UV3. For both x-ray and optical mask applications, substrates are typically coated in advance and stored until ready to use. With chemically amplified resists, the resist can not be stored for too long due to environmental contamination. Top coats are sometimes used to extend the shelf life of the resist from the time it is coated to exposure and from exposure to PEB. Experiments were done to determine if polyaniline was effective as a top coat for UV3. In these experiments, UV3 was coated with polyaniline and stored

at room temperature for various periods of time. The shelf life for the resist was 5-8 days whereas with polyaniline it was extended to at least 22 days (Figure 8). At this point the experiment was stopped.

Example 2: Polyaniline on Top of a Negative tone Photoresist CGR

Polyaniline was also found to be effectively coated on the negative resist CGR. It was found to increase the shelf life of CGR from 4 hours to 24 hours. CGR is generally less stable than the + tone UV3 resist.

Example 3: Polyaniline on Top of PMMA and SNR

Polyaniline was also tested on top of the electron beam polymethylmethacrylate (PMMA) resist and on the - tone SNR resist. In both cases, it was found that polyaniline did not contaminate the resist if it was removed prior to the PEB process.

Polyaniline has been found to be an effective top coat discharge layer. It can be applied on the resist without degradation of the resist lithography if the processing conditions and pH are well controlled. Best results are attained when polyaniline is removed before the resist PEB. The pH did not seem to have a significant effect on the resist if it was removed before the PEB. If the polyaniline is left on during the PEB, the acid in the polyaniline contaminates the resist and if too much base is added to neutralize the polyaniline acidity, the base also can contaminate the resist. It is therefore important to control the pH of the polyaniline. For best results the pH should be between 1 and 5, more preferably between 1.5 and 5 and most preferably between 1.5 and 3.

A list of resists include: UVx series (IBM/Shipley products consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers thereof with other polymerizable units such as styrene, methylmethacrylate, and so fourth, Methacrylate/acrylate polymers such as polymethylmethacrylate and derivatives thereof, SNR, CGR, KRS,Zep, silicon containing resists, PBS (polybutanesulfone), organometallic resists,novolak containing resists, novolak/diazoquinone resists, and so fourth. The resist can be + tone or - tone; it can be a single layer resist or multilayer resist; chemically amplified and non chemically amplified. The following U.S. patents describe resists useful to practice the present invention are incorporated herein by reference: 5,580,694, 5,554,485, 5,545,509, 5,492,793, 5,401,614, 5,296,332, 5,240,812, 5,071,730, 4,491,628, 5,585,220, 5,561,194, 5,547,812, 5,498,765, 5,486,267, 5,482,817, 5,464,726, 5,380,621, 5,374,500, 5,372,912, 5,342,727, 5,304,457, 5,300,402, 5,278,010, 5,272,042, 5,266,444, 5,198,153, 5,164,278, 5,102,772, 5,098,816, 5,059,512, 5,055,439, 5,047,568, 5,045,431, 5,026,624, 5,019,481, 4,940,651, 4,939,070, 4,931,379, 4,822,245, 4,800,152, 4,760,013, 4,551,418, 5,338,818, 5,322,765, 5,250,395, 4,613,398, 4,552,833, 5,457,005, 5,422,223, 5,338,818, 5,322,765, 5,312,717, 5,229,256, 5,286,599, 5,270,151, 5,250,395, 5,238,773, 5,229,256, 5,229,251, 5,215,861, 5,204,226, 5,115,095, 5,110,711, 5,059,512, 5,041,358, 5,023,164, 4,999,280, 4,981,909, 4,908,298, 4,867,838, 4,816,112, 4,810,601, 4,808,511, 4,782,008, 4,770,974, 4,693,960, 4,692,205, 4,665,006, 4,657,845, 4,613,398, 4,603,195, 4,601,913, 4,599,243, 4,552,833, 4,507,331, 4,493,855, 4,464,460, 4,430,153, 4,307,179, 4,307,178, 5,362,599, 4,397,937, 5,567,569, 5,342,727, 5,294,680, 5,273,856, 4,980,264, 4,942,108, 4,880,722, 4,853,315, 4,601,969, 4,568,631, 4,564,575, 4,552,831, 4,522,911, 4,464,458, 4,409,319, 4,377,633, 4,339,522, 4,259,430, 5,209,815, 4,211,834, 5,260,172, 5,258,264, 5,227,280, 5,024,896, 4,904,564, 4,828,964, 4,745,045, 4,692,205, 4,606,998, 4,600,683, 4,499,243, 4,567,132, 4,564,584, 4,562,091, 4,539,222, 4,493,855, 4,456,675, 4,359,522, 4,289,573, 4,284,706, 4,238,559, 4,224,361, 4,212,935,

4,204,009, 5,091,103, 5,124,927, 5,378,511, 5,366,757, 4,590,094, 4,886,727, 5,268,260, 5,391,464, 5,115,090, 5,114,826, 4,886,734, 4,568,601, 4,678,850, 4,543,319, 4,524,126, 4,497,891, 4,414,314, 4,414,059, 4,398,001, 4,389,482, 4,379,826, 4,379,833, 4,187,331.

Polyaniline was also found to be a protective conducting coating enhancing the shelf life of the resist. It basically functions by scavenging environmental contaminants that would normally diffuse into the resist.

CGR stands a negative DUV chemically amplified resist. The chemical components are poly hydroxy styrene, MDT as the photo acid generator (PAG), and powderlink as the crosslinker. SNR is a Shipley negative DUV chemically amplified resist. SNR stands for Shipley Negative Resist. It is a poly hydroxy styrene. It contains a melamine crosslinker and a PAG. KRS is a positive deep-uv chemically amplified resist. KRS stands for Ketal Resist System. The chemical components are poly hydroxy styrene, and acetal protected poly hydroxy styrene as copolymers. The PAG is tri phenyl sulfonium triflate. UV3 is an IBM/Shipley positive DUV chemically amplified resist. It contains poly hydroxy styrene and t-butly methacrylate copolymers. The PAG is t-butyl phenyl iodonium champor sulfonate. ZEP is an e-beam resist. It is not chemically amplified. It contains alpha chloro methacrylate and alpha methyl styrene copolymers.

TABLE 1:

pH of Polyaniline	Rinsed Before PEB (Post Exposure Bake) (Dose/Lithography) No Rinse	Rinsed After PEB Dose/Lithography
No Polyaniline /Resist Only (Control)		5.5 $\mu\text{C}/\text{cm}^2$; 0.25 μm Images Resolved
1.9	6 $\mu\text{C}/\text{cm}^2$; 0.25 μm Images Resolved	6 $\mu\text{C}/\text{cm}^2$; Resist Thinned: Patterns Gone (Acid
5	6 $\mu\text{C}/\text{cm}^2$; 0.25 μm Images Resolved	6 $\mu\text{C}/\text{cm}^2$; Pattern Did Not Develop (Excess Base Scavenged Acid from Resist- No Chemistry

While the present invention has been described with respect to preferred embodiments, numerous modifications, changes, and improvements will occur to those skilled in the art without departing from the spirit and scope of the invention.



-21-

CLAIMS

What is claimed is:

1. A structure comprising:

a surface;

an electrically conductive polymer disposed on said surface;

said electrically conductive polymer contains acid functionality;

said electrically conductive polymer has a predetermined pH.

2. A structure according to claim 1 wherein said electrically conductive polymer is one of a plurality of layers disposed on said surface.

3. A structure according to claim 3 wherein at least one of said plurality of layers comprises an energy sensitive material and wherein at least another of said layers comprises said electrically conductive polymer.

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4. A structure according to claim 1 wherein said electrically conductive polymer is in the form of a pattern on said surface.
5. A structure according to claim 1 wherein said pH is predetermined to be compatible with said surface.
6. A structure according to claim 5 wherein said surface is a resist material.
7. A structure according to claim 6 wherein said energy sensitive material is a resist.
8. a structure according to claim 7 wherein said resist is selected from the group consisting of a positive and a negative resist.
9. A structure according to claim 7 therein said resist is a chemically amplified resist.
10. A structure according to claim 1 wherein said energy sensitive material is sensitive to energy selected from the group consisting of electromagnetic radiation and a particle beam.
11. A structure according to claim 10 wherein said particle beam is selected from the group consisting of an electron beam and an ion beam.

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12. A structure according to claim 1 wherein said energy sensitive material is sensitive to said acid functionality.
13. A structure according to claim 1 wherein said surface is an electronic device.
14. A structure according to claim 13 wherein said electronic device is selected from the group consisting of an integrated circuit, a packaging substrate, a liquid crystal device and a light emitting diode.
15. A structure according to claim 7 wherein said resist is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate, methacrylate/acrylate polymers, and derivatives methacrylate/acrylate polymers, siliconcontaining resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;
16. A structure according to claim 1 wherein said electrically conductive polymer contains acids neutralizing functionality to provide said predetermined pH.
17. A structure according to claim 16 wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride;

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18. A structure according to claim 1 wherein said electrically conductive-polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylevevinylenees, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, poiyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

19. A structure according to claim 16 wherein said acid neutralizing functionality is selected from the group consisting of an additive to said electrically conductive polymer and a constituent of said electrically conductive polymer.

20. A structure comprising:

a surface;

a plurality of layers on said surface;

at least one of said plurality of layers comprises an energy sensitive material;

at least another of said layers comprises an electrically conductive polymer;

said electrically conductive polymer contains acid functionality;

said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality;

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said pH is predetermined to be in the range from about 1 to about 7;

said energy sensitive material is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate, methacrylate/acrylate polymers, and derivatives methacrylate/acrylate polymers, siliconcontaining resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride;

said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

21. A method comprising:

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disposing on a surface an electrically conductive polymer;

said electrically conductive polymer contains acid functionality;

said electrically conductive polymer has a predetermined pH.

22. A method according to claim 21 further including disposing at least another layer on said surface to form a plurality of layers disposed on said surface.

23. A method according to claim 22 wherein at least one of said plurality of layers comprises an energy sensitive material and wherein at least another of said layers comprises said electrically conductive polymer.

24. A method according to claim 21 wherein said electrically conductive polymer is in the form of a pattern on said surface.

25. A method according to claim 21 wherein said pH is predetermined to be compatible with said surface.

26. A method according to claim 25 wherein said surface is a resist material.

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-27-

27. A method according to claim 26 wherein said energy sensitive material is a resist.
28. A method according to claim 27 wherein said resist is selected from the group consisting of a positive and a negative resist.
29. A method according to claim 27 therein said resist is a chemically amplified resist.
30. A method according to claim 21 wherein said energy sensitive material is sensitive to energy selected from the group consisting of electromagnetic radiation and a particle beam.
31. A method according to claim 30 wherein said particle beam is selected from the group consisting of an electron beam and an ion beam.
32. A method according to claim 31 wherein said energy sensitive material is sensitive to said acid functionality.
33. A method according to claim 31 wherein said surface is an electronic device.
34. A method according to claim 33 wherein said electronic device is selected from the group consisting of an integrated circuit, a packaging substrate, a liquid crystal device and a light emitting diode.
35. A method according to claim 37 wherein said resist is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate,

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methacrylate/acrylate polymers, and derivatives methacrylate/acrylate polymers, siliconcontaining resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

36. A method according to claim 21 wherein said electrically conductive polymer contains acids neutralizing functionality to provide said predetermined pH.

37. A method according to claim 36 wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride;

38. A structure according to claim 21 wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

39. A structure according to claim 36 wherein said acid neutralizing functionality is selected from the group consisting of an additive to said electrically conductive polymer and a constituent of said electrically conductive polymer.

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40. A method comprising:

disposing on a surface a plurality of layers ;

at least one of said plurality of layers comprises an energy sensitive material;

at least another of said layers comprises an electrically conductive polymer;

said electrically conductive polymer contains acid functionality;

said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality;

said pH is predetermined to be in the range from about 1 to about 7;

said energy sensitive material is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate, methacrylate/acrylate polymers, and derivatives methacrylate/acrylate polymers, siliconcontaining resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine,

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pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride;

said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

41. A method according to claim 23 further including heating said energy sensitive material and removing said electrically conductive polymer prior to said heating.

42. A method according to claim 23 further including heating.

43. A method according to claim 42 wherein said conductive polymer is removed prior to said heating.

44. A method according to claim 42 wherein said conductive polymer is removed after said heating.

45. A method according to claim 23 wherein said electrically conductive polymer is removed during development of said energy sensitive material.

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46. A method according to claim 23 wherein said electrically conductive polymer is removed before development of said energy sensitive material.

47. A structure according to claim 1 further including an energy sensitive material between said electrically conductive polymer and said surface, said electrically conductive polymer provides a protective top coat to said energy sensitive material thereby increasing the shelf life of the energy sensitive material.

48. A structure according to claim 1 wherein said electrically conductive polymer is water soluble.

50. A composition of matter comprising an electrically conductive polymer having a controlled pH.

51. A composition of matter according to claim 50 wherein said composition of matter further includes an additive to provide said controlled pH.

52. A composition of matter according to claim 51 wherein said additive is an acid neutralizing additive.

53. A composition of matter according to claim 52 wherein said additive is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide,

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-32-

triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, sodium hydride.

54 A composition of matter according to claim 48 wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

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COMPOSITIONS OF MATTER, RESIST STRUCTURES INCLUDING A LAYER OF
ELECTRICALLY CONDUCTIVE POLYMER HAVING CONTROLLED pH AND
METHODS OF FABRICATION THEREOF

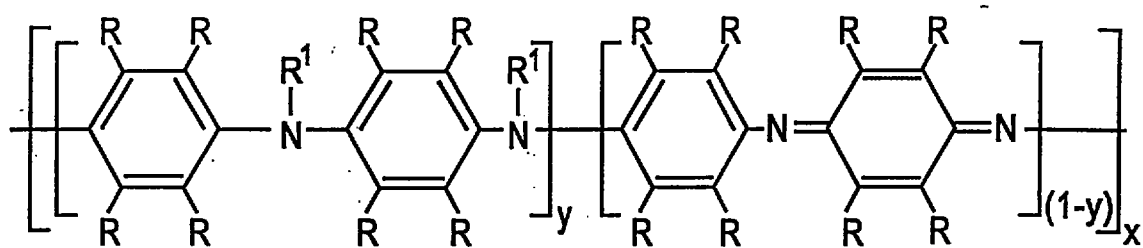
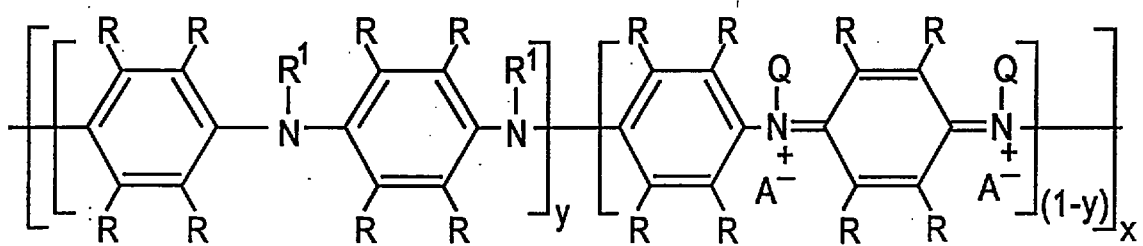
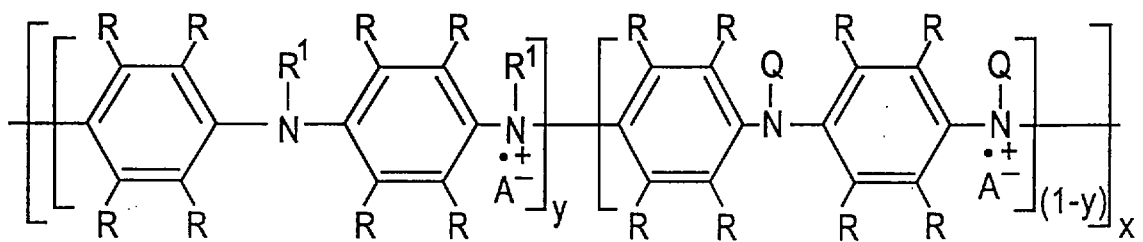
ABSTRACT

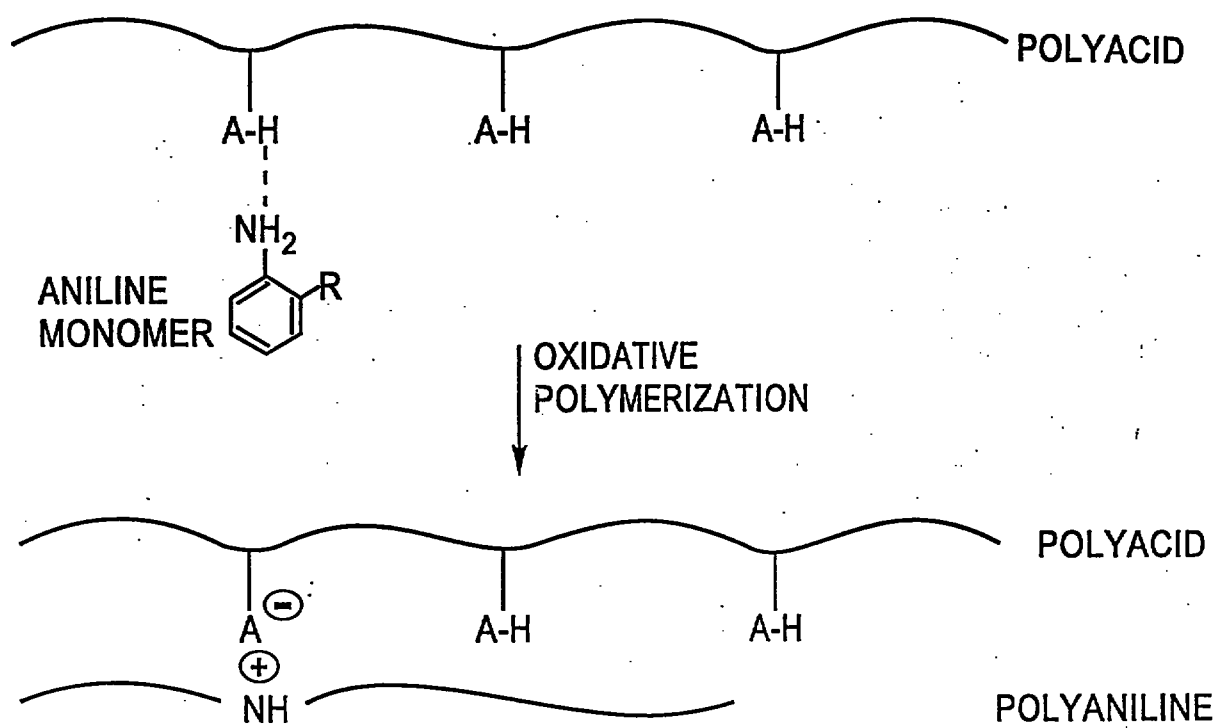
The present invention is an electrically conductive polymeric composition having a controlled pH and structures fabricated therewith and methods of fabrication thereof having: a surface; a plurality of layers on the surface; at least one of the plurality of layers is formed from an energy sensitive material; at least another layer is formed from an electrically conductive polymer, the electrically conductive polymer contains acid functionality; and the electrically conductive polymer has a predetermined pH. The pH is controlled by additives mixed in with the electrically conductive polymer or by constituents on the electrically conductive polymer. The structures are useful for lithography in microelectronic fabrication to avoid the effects of charging on resist from electron beams, and in applications as static dissipation, electromagnetic interference shielding, corrosion protection, electroplating, and wiring.

Fig 1C

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**Fig. 1A****Fig. 1B****Fig. 1C**

**Fig. 2**

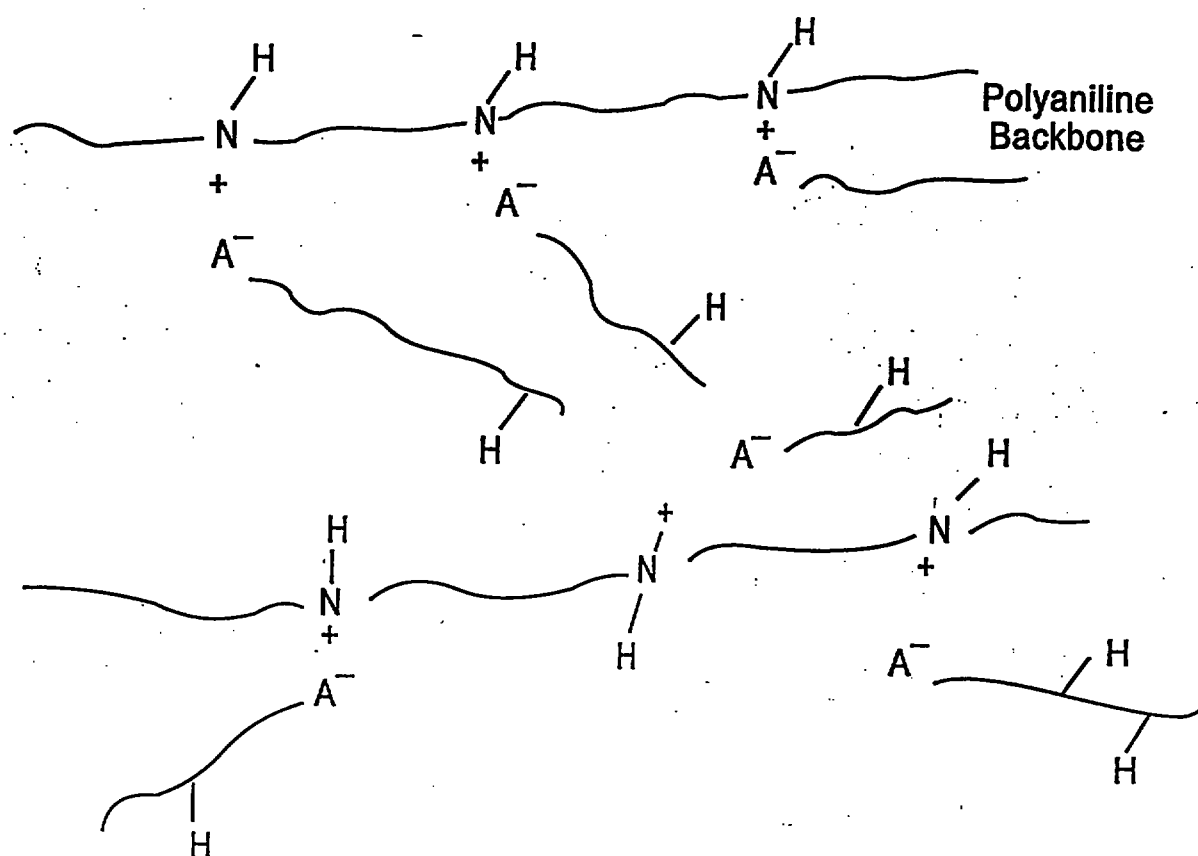
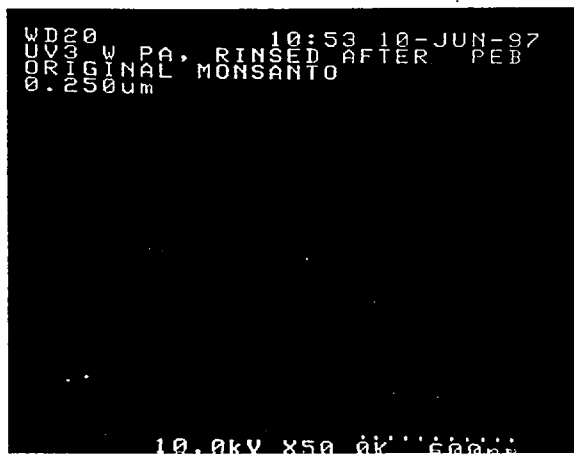


Fig. 3

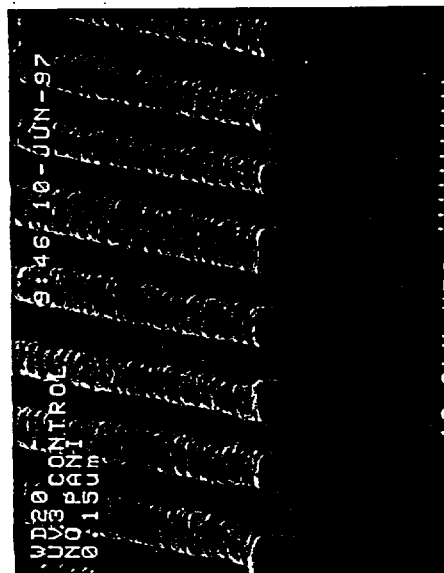
UV3 with Polyaniline No PAB, Rinsed after PEB

Ployaniline pH 1.9, 250nm features

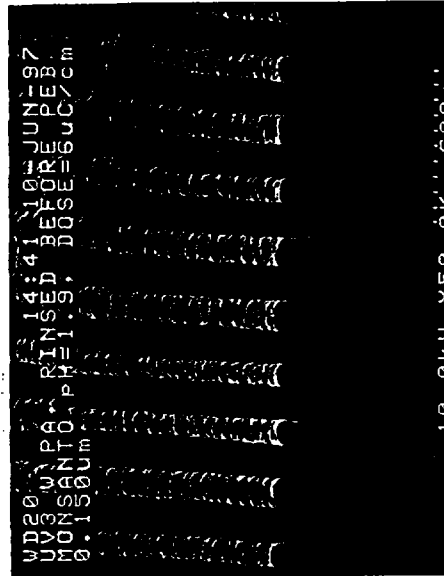


UV3 with Polyaniline No PAB, Rinsed before PEB, 150nm features

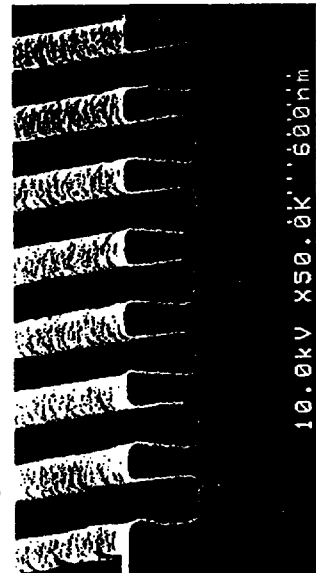
Control, No Polyaniline



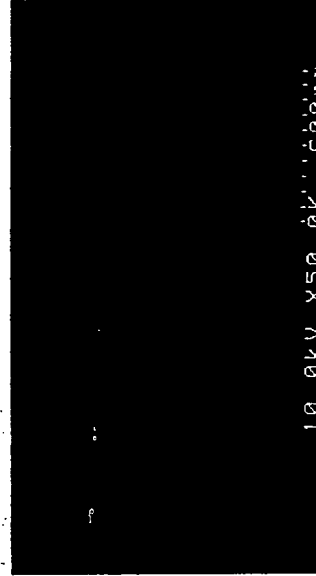
Polyaniline pH 1.9



Polyaniline pH 2.5



Polyaniline pH 5.0



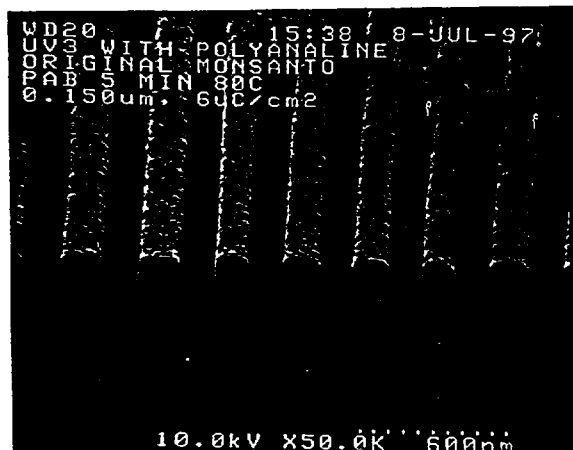
UV3 with Polyaniline PAB 5 minutes at 80°C

pH 1.9, 150nm features



UV3 with Polyaniline PAB 5 minutes at 80°C

pH 2.5, 150nm features



UV3 Shelf Life with and without Polyaniline

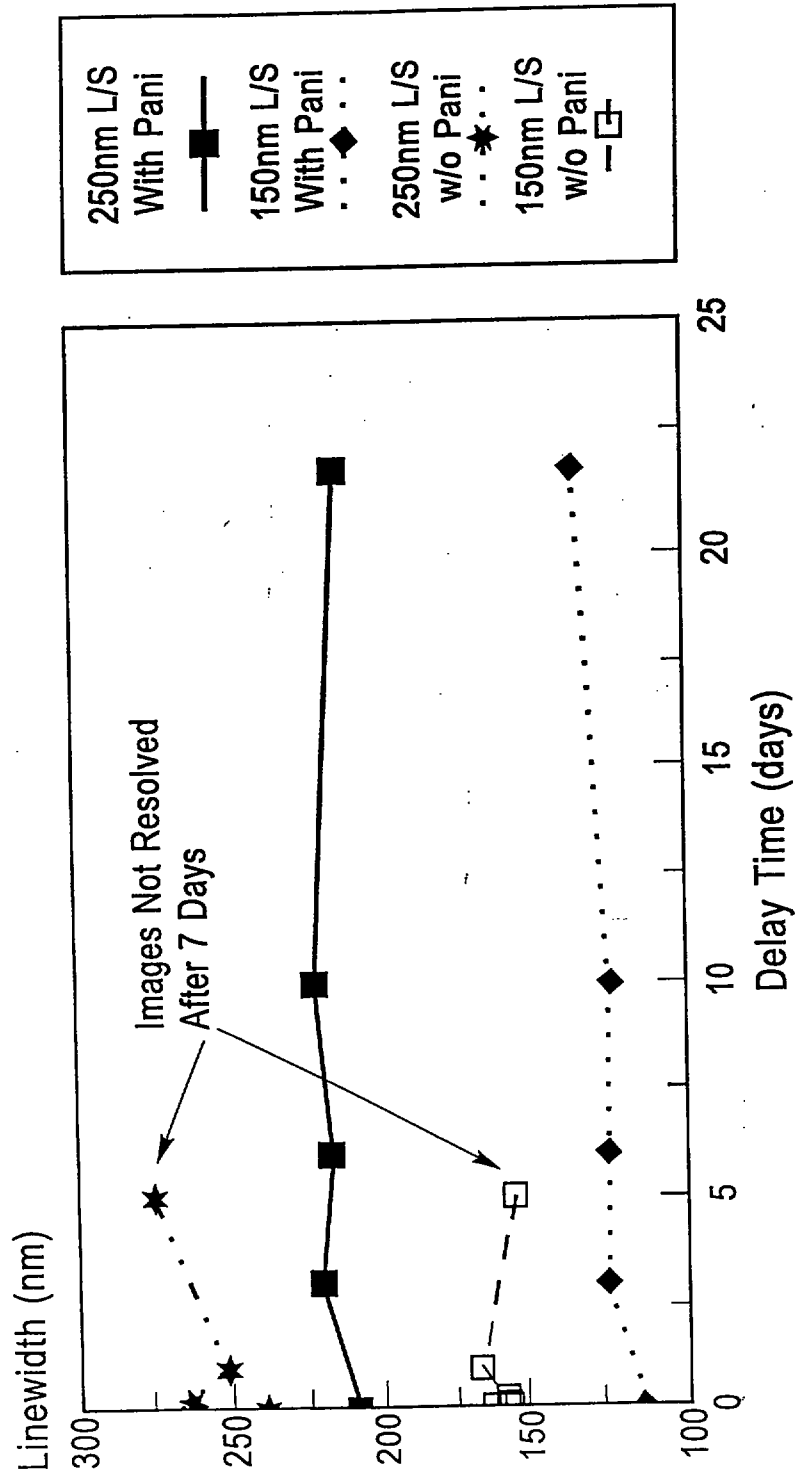


Fig. 8

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layer in the exposed regions so that either the exposed or unexposed regions can be subsequently removed to form a pattern in the energy sensitive layer. In positive acting resists the exposed regions become soluble whereas in negative acting resists the exposed regions become insoluble. In either case a pattern has been generated in the resist or energy sensitive layer. This pattern can then be transferred down to underlying layers by various etching mechanisms.

Where the pattern of energy results in generation of electrical charge or carries an electrical charge, electrical charge can in turn accumulate at the energy sensitive layer or in the underlying layers which can result in distortion of the pattern being created in the energy sensitive layer. Such distortions create huge image placement variations and errors. This occurs when a dielectric energy sensitive material such as a resist is exposed to a charged beam such as an electron beam or an ion beam. The dielectric energy sensitive layer accumulates charge from the beam. The accumulated charge introduces electric fields which after reaching a sufficient magnitude distorts the beam and results in a misplacement of the beam on the energy sensitive material. This creates errors in the pattern being formed in the layer.

This can be avoided by disposing on, under or within the energy sensitive layer a layer of electrically conductive material which can be used to drain off the accumulated charge and remove or reduce the undesired electric field.

Electrically conductive organic polymers are a class of electronic materials that combine the electrical properties of metals with the processability and mechanical properties characteristic of polymers. Examples of such polymers include polyparaphenylene vinylenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfuranes,

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Another more particular aspect of the present invention is a method of disposing on a surface a plurality of layers; at least one of the plurality of layers is formed from an energy sensitive material; at least another layer is formed from an electrically conductive polymer; the electrically conductive polymer contains acid functionality; and the electrically conductive polymer has a predetermined pH.

More specifically, there is provided according to a first embodiment of the invention a structure comprising:

- a surface;
- an electrically conductive polymer disposed on said surface;
- wherein said electrically conductive polymer contains acid functionality;
- wherein said electrically conductive polymer has a predetermined pH to be a predetermined value;
- wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant, said dopant dopes said precursor to be electrically conductive;
- wherein said electrically conductive polymer comprises an additive to provide said predetermined pH which is different than the pH of said electrically conductive polymer without said additive.

According to a second embodiment of the invention there is provided a structure comprising:

- a surface;
- a plurality of layers on said surface;
- at least one of said plurality of layers comprises an energy sensitive material;
- at least another of said layers comprises an electrically conductive polymer;

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wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant comprising acid neutralizing functionality;

wherein said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality;

wherein said pH is predetermined to be in the range from about 1 to about 7;

wherein said energy sensitive material is selected from the group consisting of

hydroxystyrene/t-butylmethacrylate copolymers,

hydroxystyrene/t-butylmethacrylate terpolymers,

hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate,

methacrylate/acrylate polymers, methacrylate/acrylate derivatives,

methacrylate/acrylate polymers,

silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, and sodium hydride;

wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

According to a third embodiment of the invention there is provided a method comprising:

- disposing on a surface an electrically conductive polymer;
- wherein said electrically conductive polymer contains acid functionality;
- wherein said electrically conductive polymer has a predetermined pH;
- wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant, said dopant dopes said precursor to be electrically conductive;

- wherein said electrically conductive polymer contains an additive to provide said predetermined pH which is different than the pH of said electrically conductive polymer without said additive.

According to a fourth embodiment of the invention there is provided a method comprising:

- disposing on a surface a plurality of layers;
- at least one of said plurality of layers comprises an energy sensitive material;
- at least another of said layers comprises an electrically conductive polymer;
- said electrically conductive polymer contains acid functionality;
- said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality, said pH is different than the pH of said electrically conductive polymer without said additive;

- said pH is predetermined to be in the range from about 1 to about 7;

- said energy sensitive material is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers,

- hydroxystyrene/t-butylmethacrylate terpolymers, hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate,

11 FEB 2000

methacrylate/acrylate polymers, methacrylate/acrylate derivatives,

methacrylate/acrylate polymers,

silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, and sodium hydride;

said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

Brief Description of the Drawings

Further objects, features, and advantages of the present invention will become apparent from a consideration of the following detailed description of the invention when read in conjunction with the drawing FIGs., in which:

Fig. 1 is a general formula for a polyaniline; (a) is the precursor form of the polymer or the non-doped form of the polymer; (b) is the doped form of the polymer or the electrically conducting form of polyaniline; (c) is the actual structure for the doped electrically conducting polymer consisting of a polysemiquinone radical cation.

Fig. 2 depicts the structure of the water soluble polyacid/polyaniline material.

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Fig. 3 depicts electrically conducting polyaniline having excess acid functionality.

Fig. 4 depicts .25 um features delineated with UV3 containing polyaniline with a pH of 1.9 on top. The polyaniline was left in place during the resist post exposure bake. As can be seen, severe thinning is observed due to acid contamination from the polyaniline into the resist.

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-7-

Figs. 5a, 5b 5c and 5d (for polyaniline, pH = 1.9, pH = 2.5 and pH = 5.0, respectively) depict .15um features with polyaniline of various pHs on UV3 resist. The polyaniline is removed before the PEB in all cases. Lithography of the resist looks good, indicating that there is no contamination issues.

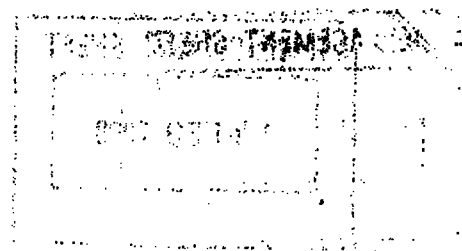
Fig. 6 depicts polyaniline with pH of 1.9 on UV3. The polyaniline is post apply baked at 80 C for 5 minutes. There is no effect on resist lithography is observed due to the polyaniline bake.

Fig. 7 depicts polyaniline with pH of 2.5 on UV3. The polyaniline is post apply baked at 80 C for 5 minutes. There is no effect on resist lithography is observed due to the polyaniline bake.

Fig. 8 depicts the shelf life of UV3 with and without polyaniline top coat. As can be seen, the polyaniline extends the shelf life of the polymer to 24 days at which time the experiment was stopped.

DETAILED DESCRIPTION

The present invention is directed to electrically conducting polymers having controlled pH and to structures fabricated therewith. Examples of such polymers that can be used to practice the present invention are of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and copolymers of monomers thereof. The general formula for these polymers can be found



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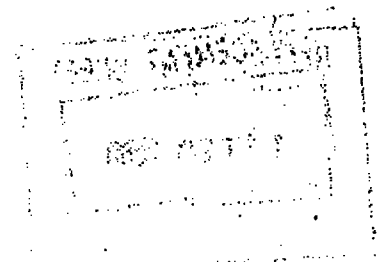
hydroxide. The emeraldine base is then filtered, washed with ammonium hydroxide, then washed with methanol and dried. The polymer at this stage is in the undoped emeraldine base form as a powder.

Substituted (either on the aromatic ring or on the nitrogen) polyanilines in the emeraldine form are synthesized in the same fashion as above but using the appropriate substituted aniline monomer in the polymerization reaction. Copolymers are made by the oxidation polymerization of one or more monomers. Other acids can also be used in the polymerization reaction other than hydrochloric acid. Aqueous acetic acid, sulfuric acid, organic sulfonic acids, such as aqueous toluenesulfonic acid, dodecylbenzenesulfonic acid, camphorsulfonic acid, and so on. The o-ethoxy substituted polyaniline was prepared by oxidative polymerization of o-ethoxy aniline in 1N hydrochloric acid as described above. Copolymers having various amounts of o-ethoxy content were synthesized by polymerizing o-ethoxyaniline and aniline in aqueous 1N hydrochloric acid. The amount of o-ethoxy content in the final polymer was controlled by varying the feed ratio of this monomer in the initial polymerization reaction ("o-" as used herein means the ortho-ring position).

The substituted and unsubstituted emeraldine base powder is generally processed by dissolving the powder in an organic solvent. The unsubstituted emeraldine base was dissolved in NMP (N-methylpyrrolidinone) at a 5-10% concentration or DMPU (dimethylpropylene urea). The solution can be used to spin-coat films of the emeraldine base polymer on silicon wafers, quartz wafers, salt plates, and so on. These films were on the order of 500 Å to 1.0 µm. Thicker films (on the order of 50 to 200 µm) were made by solution casting techniques in which the solution was poured into an aluminium pan or glass dish and placed into a vacuum oven at 60° C for 24 hours. The solution can also be

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used to process the material into a structural part or into a fiber. The substituted
emeraldine base such as the o-ethoxy





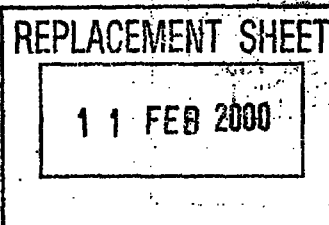
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What is claimed is:

1. A structure comprising:
 - a surface;
 - an electrically conductive polymer disposed on said surface;
 - wherein said electrically conductive polymer contains acid functionality;
 - wherein said electrically conductive polymer has a predetermined pH to be a predetermined value;
 - wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant, said dopant dopes said precursor to be electrically conductive;
 - wherein said electrically conductive polymer comprises an additive to provide said predetermined pH which is different than the pH of said electrically conductive polymer without said additive.
2. A structure according to claim 1 wherein said electrically conductive polymer is one of a plurality of layers disposed on said surface.
3. A structure according to claim 2 wherein at least one of said plurality of layers comprises an energy sensitive material and wherein at least another of said layers comprises said electrically conductive polymer.
4. A structure according to any one of claims 1-3 wherein said electrically conductive polymer is in the form of a pattern on said surface.
5. A structure according to any one of claims 1-4 wherein said pH is predetermined to be compatible with said surface.
6. A structure according to claim 5 wherein said surface is a resist material.
7. A structure according to claim 6 wherein said resist is an energy sensitive material.
8. A structure according to claim 7 wherein said resist is a positive resist.



9. A structure according to claim 7 wherein said resist is a chemically amplified resist.
10. A structure according to any one of claims 1-5 wherein said surface is sensitive to energy selected from the group consisting of electromagnetic radiation and a particle beam.
11. A structure according to claim 10 wherein said particle beam is selected from the group consisting of an electron beam and an ion beam.
12. A structure according to any one of claims 1-5 wherein said surface is sensitive to said acid functionality.
13. A structure according to any one of claims 1-5 wherein said surface is an electronic device.
14. A structure according to claim 13 wherein said electronic device is selected from the group consisting of an integrated circuit, a packaging substrate, a liquid crystal device and a light emitting diode.
15. A structure according to claim 7 wherein said resist is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate, methacrylate/acrylate polymers, and derivatives, methacrylate/acrylate polymers, silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists.
16. A structure according to any one of claims 1-15 wherein said additive is an acid neutralizing functionality to provide said predetermined pH.
17. A structure according to claim 16 wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine,





t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary amines, secondary amines, tertiary amines, proton sponge, sodium hydride.

18. A structure according to any one of claims 1-17 wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

19. A structure comprising:

a surface;

a plurality of layers on said surface;

at least one of said plurality of layers comprises an energy sensitive material;

at least another of said layers comprises an electrically conductive polymer;

wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant comprising acid neutralizing functionality;

wherein said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality;

wherein said pH is predetermined to be in the range from about 1 to about 7;

wherein said energy sensitive material is selected from the group consisting of

hydroxystyrene/t-butylmethacrylate copolymers,

hydroxystyrene/t-butylmethacrylate terpolymers,

hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate,

methacrylate/acrylate polymers, methacrylate/acrylate derivatives,

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methacrylate/acrylate polymers,

silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, and sodium hydride;

wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

20. A method comprising:

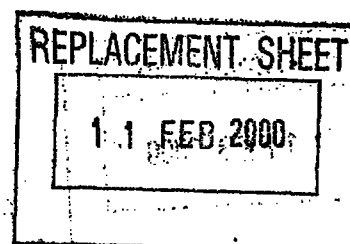
disposing on a surface an electrically conductive polymer;

wherein said electrically conductive polymer contains acid functionality;

wherein said electrically conductive polymer has a predetermined pH;

wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant, said dopant dopes said precursor to be electrically conductive;

wherein said electrically conductive polymer contains an additive to provide said predetermined pH which is different than the pH of said electrically conductive polymer without said additive.





21. A method according to claim 20 further including disposing at least another layer on said surface to form a plurality of layers disposed on said surface.
22. A method according to claim 21 wherein at least one of said plurality of layers comprises an energy sensitive material and wherein at least another of said layers comprises said electrically conductive polymer.
23. A method according to any one of claims 20-22 wherein said electrically conductive polymer is in the form of a pattern on said surface.
24. A method according to any one of claims 20-23 wherein said pH is predetermined to be compatible with said surface.
25. A method according to claim 24 wherein said surface is a resist material.
26. A method according to claim 25 wherein said resist is an energy sensitive material.
27. A method according to claim 26 wherein said resist is a positive resist.
28. A method according to claim 26 wherein said resist is chemically amplified resist.
29. A method according to any one of claims 20-24 wherein said surface is sensitive to energy selected from the group consisting of electromagnetic radiation and a particle beam.
30. A method according to claim 29 wherein said particle beam is selected from the group consisting of an electron beam and an ion beam.
31. A method according to claim 22 wherein said energy sensitive material is sensitive to said acid functionality.
32. A method according to claim 30 wherein said surface is an electronic device.
33. A method according to claim 32 wherein said electronic device is selected from the group consisting of an integrated circuit, a packaging substrate, a liquid crystal device and a light emitting diode.
34. A method according to claim 26 wherein said resist is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers and terpolymers.

REPLACEMENT SHE

11 FEB 2000



hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate, methacrylate/acrylate polymers, and derivatives, methacrylate/acrylate polymers, silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists.

35. A method according to any one of claims 20-34 wherein said electrically conductive polymer contains acid neutralizing functionality to provide said predetermined pH.

36. A method according to claim 35 wherein said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary amines, secondary amines, tertiary amines, proton sponge, and sodium hydride.

37. A method according to any one of claims 20-36 wherein said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

38. A method comprising:

disposing on a surface a plurality of layers;

at least one of said plurality of layers comprises an energy sensitive material;

at least another of said layers comprises an electrically conductive polymer;

said electrically conductive polymer contains acid functionality;

REPLACEMENT SHEET

17 FEB 2000



said electrically conductive polymer has a predetermined pH provided by acid neutralizing functionality, said pH is different than the pH of said electrically conductive polymer without said additive;

said pH is predetermined to be in the range from about 1 to about 7;

said energy sensitive material is selected from the group consisting of hydroxystyrene/t-butylmethacrylate copolymers,

hydroxystyrene/t-butylmethacrylate terpolymers, hydroxystyrene/t-butylmethacrylate copolymers with styrene and methylmethacrylate,

methacrylate/acrylate polymers, methacrylate/acrylate derivatives,

methacrylate/acrylate polymers,

silicon containing resists, polybutanesulfone, organometallic resists, novolak containing resists and novolak/diazoquinone resists;

said acid neutralizing functionality is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary, secondary and tertiary amines, proton sponge, and sodium hydride;

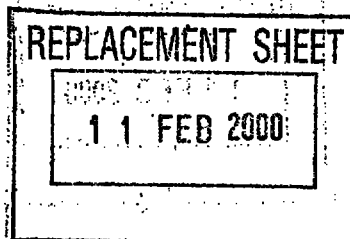
said electrically conductive polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylene vinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof, blends thereof with other polymers and copolymers of the monomers thereof.

REPLACEMENT SHEET

11 FEB 2000



39. A method according to claim 22 further including heating.
40. A method according to claim 39 wherein said conductive polymer is removed prior to said heating.
41. A method according to claim 39 wherein said conductive polymer is removed after said heating.
42. A method according to claim 22 wherein said electrically conductive polymer is removed during development of said energy sensitive material.
43. A method according to claim 22 wherein said electrically conductive polymer is removed before development of said energy sensitive material.
44. A structure according to any one of claims 1 to 18 further including an energy sensitive material between said electrically conductive polymer and said surface, said electrically conductive polymer provides a protective top coat to said energy sensitive material thereby increasing the shelf life of the energy sensitive material.
45. A structure according to any one of claims 1 to 17 wherein said electrically conductive polymer is water soluble.
46. A composition of matter comprising an electrically conductive polymer having a predetermined pH, wherein said electrically conductive polymer comprises a precursor to an electrically conductive polymer and a dopant, wherein said dopant dopes said precursor to be electrically conductive;
- wherein said electrically conductive polymer comprises an additive to provide said predetermined pH which is different than the pH of said electrically conductive polymer without said additive.
47. A composition of matter according to claim 46 wherein said composition of matter further includes an additive to provide said controlled pH.





48. A composition of matter according to claim 47 wherein said additive is an acid neutralizing additive.

49. A composition of matter according to claim 47 or claim 48 wherein said additive is selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, triethylamine, pyridine, t-butoxide, morpholine, pyrrolidinone, potassium hydroxide, sodium hydroxide, lithium hydroxide, triphenylsulfonium hydroxide, primary amines, secondary amines, tertiary amines, proton sponge, sodium hydride.

50. A structure according to claim 7 wherein said resist is a negative resist.

51. A structure according to claim 26 wherein said resist is a negative resist.

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11 FEB 2000

COMPOSITIONS OF MATTER, RESIST STRUCTURES INCLUDING A
LAYER OF ELECTRICALLY CONDUCTIVE POLYMER HAVING
CONTROLLED pH AND METHODS OF FABRICATION THEREOF

ABSTRACT OF THE DISCLOSURE

The present invention is an electrically conductive polymeric composition of matter having a controlled pH and structures fabricated therewith and methods of fabrication thereof having: a surface; a plurality of layer on the surface; at least one of the plurality of layers is formed from an energy sensitive material; at least another layer is formed from an electrically conductive polymer, the electrically conductive polymer contains acid functionality; and the electrically conductive polymer has a predetermined pH. The pH is controlled by additives mixed in with the electrically conductive polymer or by constituents on the electrically conductive polymer. The electrically conductive polymer is preferably a top layer. The structures are useful for lithography in microelectronic fabrication to avoid the effects of charging on resist from electron beams. The compositions are also useful in applications as static dissipation, electromagnetic interference shielding, corrosion protection, electroplating, and wiring.

