

Conducting polymers in microelectronics

by M. Angelopoulos

Conjugated polymers in the nondoped and doped conducting state have an array of potential applications in the microelectronics industry. Conducting polymers are effective discharge layers as well as conducting resists in electron beam lithography, find applications in metallization (electrolytic and electroless) of plated through-holes for printed circuit board technology, provide excellent electrostatic discharge protection for packages and housings of electronic equipment, provide excellent corrosion protection for metals, and may have applications in electromagnetic interference shielding. This paper reviews some of these applications and briefly describes possible future applications of conducting polymers for use as interconnections or for electronic devices.

Introduction

Microelectronics, the industry of information processing, has revolutionized our technological society. Electronic products in the form of home entertainment equipment, mobile electronic devices, desktop personal computers, and large supercomputers are pervasive in our everyday world. The electronics revolution began in the 1960s with the fabrication of the first integrated circuits (ICs) [1]. Since then, this industry has experienced remarkable growth resulting in significantly more complex ICs which are faster and smaller, and whose cost per function has decreased [2–9].

Conductors, semiconductors, and insulators, materials comprising the entire spectrum of conductivity, are integral to integrated circuit processing [6, 9, 10–12]. The active device components are composed of semiconductors. Conductors are extensively used for interconnection applications, for electrostatic discharge (ESD) protection of ICs, and for electromagnetic interference (EMI) shielding of electronic equipment. Insulators, most commonly polymers, are widely used as interlevel dielectrics, encapsulants, and materials for the packaging and housing of electronic equipment [6, 10–12].

Conducting polymers [13] offer a unique combination of properties that make them attractive alternatives for certain materials currently used in microelectronics. These polymers are made conducting, or “doped,” by reacting the conjugated semiconducting polymer with an oxidizing agent, a reducing agent, or a protonic acid, resulting in highly delocalized polycations or polyanions [13]. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping, and by blending with other polymers. In addition, polymeric materials are lightweight, easily processed, and flexible.

Conducting polymers have potential applications at all levels of microelectronics (see **Figure 1**). This paper examines the use of conducting polymers in the area of lithography, with a subsequent discussion of their use for metallization, as corrosion-protecting coatings for metals, and as ESD-protective coatings for packages and housings of electronic equipment. Two areas of application for conducting polymers in the future are mentioned: their possible use in interconnection technology and as novel organic materials in electronic devices.

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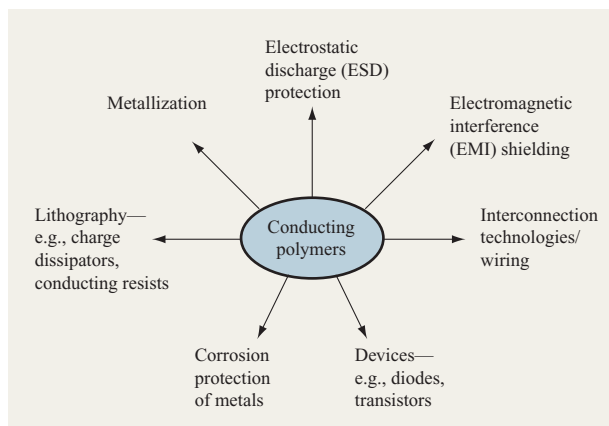


Figure 1

Overview of some of the potential applications of conducting polymers in microelectronics.

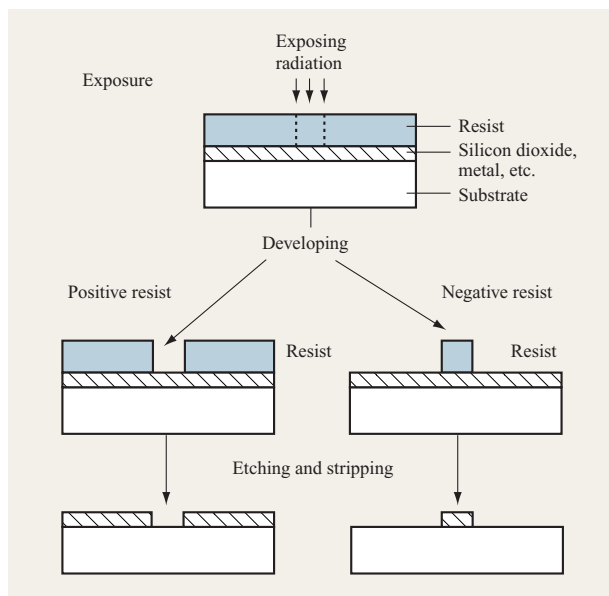


Figure 2

Schematic depicting pattern delineation by lithography.

Lithography

Background

Lithographic techniques delineate the intricate patterns necessary to form the doped regions of silicon on a chip, or their interconnections, or the interconnections on a package [4, 5, 12, 14]. Lithography relies on radiation-sensitive polymers called resists which, when irradiated through a quartz/chrome mask containing the pattern to

be transferred, undergo chain-scissioning, cross-linking, deprotection, or molecular rearrangement, thereby creating a difference in solubility between the irradiated or exposed areas and the non-irradiated or unexposed areas of the polymer [4, 5, 12, 14]. In a subsequent step, called *develop*, the more soluble regions of the resist are selectively removed, as shown in **Figure 2**. This pattern is subsequently transferred to the underlying substrate (e.g., silicon dioxide, silicon nitride, silicon, or metal) by various etching processes, followed by removal of the resist [4, 5, 15].

Resists may be patterned with photons at different wavelengths (365 nm, 248 nm, 193 nm), electron beams, X-rays, and ion beams [16–18]. Photolithography has been the dominant technology in the industry to date. However, electron-beam (e-beam) technology is used to fabricate masks for photolithography [4] and for high-resolution, low-volume specialty chips, and it is currently being considered as a next-generation projection lithography option for semiconductor device fabrication [19].

The dimensions that must be delineated are rapidly decreasing. Current DRAM and logic devices require minimum feature size dimensions of less than 150 nm [16, 17]. As the industry continues to require improved resolution, new materials, processes, and tools must evolve to sustain this trend.

Charge dissipators for electron-beam lithography

E-beam lithography is a direct-write method in which a focused beam of electrons is directly scanned over the resist [4, 5, 17, 18]; no mask is required because the pattern is computer-generated. It is a technology capable of extremely high resolution, since the beam of electrons can be focused to tens of nanometers [18], and capable also of excellent alignment of level-to-level pattern overlays. Recently, electron projection lithography has received considerable attention as a potential next-generation lithography option [16, 19].

During the e-beam patterning process, charging of the resist can be problematic [20–22]. Insulating resist materials trap charge and delay its bleed-off through the underlying silicon. The trapped charge and surface charge can deflect the path of the electron beam and result in image distortion as well as errors in level-to-level registration. To circumvent this problem, conducting materials which function as discharge layers are incorporated into resist systems as coatings above or below the imaging resist. Indium–tin-oxide films [23], amorphous carbon films produced by plasma chemical vapor deposition [24], and thin metal coatings [5, 25] can eliminate charging. However, these solutions are not ideal, since evaporative processes are needed to deposit the films. The actual conditions of evaporation may generate heat or stray irradiation, degrading the lithographic

performance of the resist. In addition, the subsequent removal of these layers is difficult if not impossible.

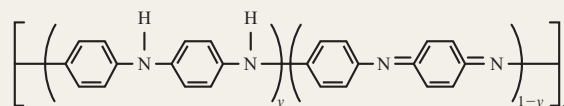
The ionically conducting, water-soluble ammonium poly(p-styrenesulfonate) [26, 27] has also been reported as a charge dissipator for e-beam lithography. It has the advantage of ease of processability, since it can be spin-applied. However, its conductivity is low, and thus its effectiveness at eliminating resist charging is marginal [28].

Conducting polymers, particularly the soluble derivatives, are attractive alternative charge dissipators for e-beam lithography. These materials combine high conductivity with ease of processability. The first conducting polymer to be evaluated in this type of application is polyaniline [29]. Polyaniline refers to a class of polymers which in the nonconducting or base form have the general composition depicted in **Structure 1** [30–35].

These materials are generally doped with protonic acids such as aqueous hydrochloric acid (HCl) to give a conductivity of the order of 1 S/cm^2 [30–32]. Polyanilines, from an industrial point of view, are the preferred conducting polymer system for many applications, since this family of polymers offer a number of advantages over other conducting polymers. They are generally soluble [36–39], environmentally stable polymers that are fabricated by a one-step synthesis involving inexpensive raw materials [40]. They offer extensive chemical versatility, allowing the properties of the polymer to be tuned to more appropriately meet the needs of a given application. Indeed, many polyaniline derivatives exist today as a result of chemical modification of their polymer backbone [32, 41–46], the introduction of dopant [47–51], or changes in their oxidation state [32, 52, 53].

When polyaniline was first evaluated as an e-beam discharge layer [29], the polymer was incorporated into a multilayer resist system (**Figure 3**) as a conducting interlayer between the imaging resist and a planarizing underlayer. The multilayer structure was designed to test the efficiency of the conducting polyaniline as charge dissipator. For this reason, a relatively thick layer of insulator which would tend to enhance charging was used. The underlayer consisted of a $2.8\text{-}\mu\text{m}$ film of a hard-baked or cross-linked novolak resin such as the AZ4210 resist material and 500 nm of silicon dioxide. Polyaniline in the base form (200 nm) was spin-applied onto the resist. The base polymer was then doped by dipping the sample into a dilute aqueous hydrochloric acid solution. Because this particular conducting salt is insoluble, the resist (a typical diazonaphthoquinone-novolac formulation [4]) could be coated directly on top of the polyaniline without interfacial problems.

This multilayer structure was then subjected to an electron beam to evaluate resist charging during the e-beam writing process. Initially, a 20×20 matrix of $2\text{-}\mu\text{m}$



Structure 1

Basic (nonconducting) form of polyaniline-type polymer.

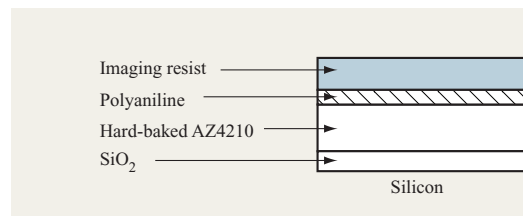


Figure 3

Multilayer resist system incorporating polyaniline as a conducting interlayer.

squares was written across a 5-mm chip. (Because of its low density, charging during the writing of this pattern is negligible.) The chip was then completely overwritten except for a $10\text{-}\mu\text{m} \times 10\text{-}\mu\text{m}$ area centered around each inner square, as illustrated in **Figure 4**. This exposure was performed on a 25-keV e-beam system. Following exposure, the resist was developed, and the images were inspected to determine the degree of pattern displacement.

In this test, the low-density pattern (inner squares) is used as a reference. When no charging occurs, the $2\text{-}\mu\text{m}$ squares are located at the center of the $10\text{-}\mu\text{m}$ squares, as shown in **Figure 5**. However, as charging occurs during the writing of the dense second pattern, the e-beam is offset with respect to the first reference pattern; as a result, the squares are no longer centered. In general, the first square written is least affected by charging, since only a small area has been written, whereas the last square written is strongly influenced by charging because of the high density of exposed area. The displacement, observed from the first to the last squares written and measured by taking the difference between the centers of the inner and outer squares, is directly related to charging (**Figure 5**).

A pattern displacement greater than $5 \text{ }\mu\text{m}$ across a 5-mm chip was observed when a conducting discharge layer was not incorporated into the resist structure (**Figure 6**), whereas use of a polyaniline layer reduced the displacement to zero (**Figure 7**) [29]. These results demonstrate that polyaniline is very effective at

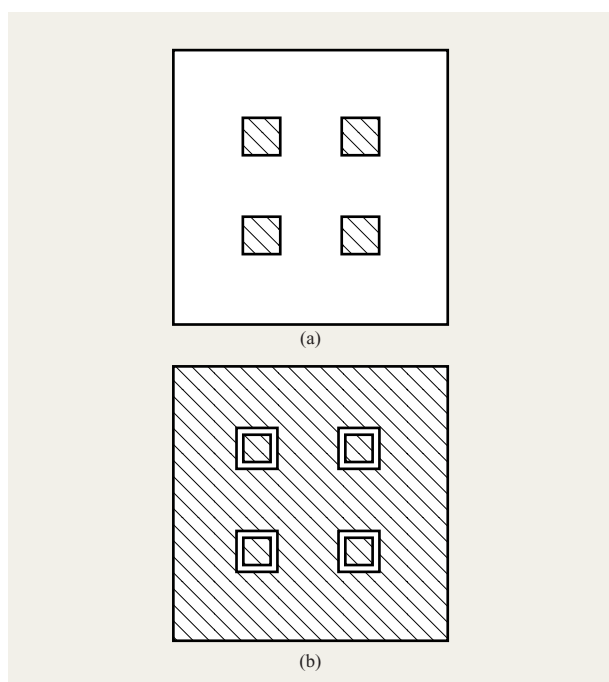


Figure 4

E-beam discharge test pattern: (a) 20×20 matrix of $2\text{-}\mu\text{m}$ squares is written; (b) the rest of the chip is written, except for $10\text{-}\mu\text{m}$ squares around the inner $2\text{-}\mu\text{m}$ squares. (From [29].)

eliminating resist charging, even though it is used as a thin interlayer between thick insulating layers in this nongrounded configuration; however, the silicon wafer substrate is grounded with connections made at the top and bottom surfaces of the wafer. The polyaniline functions by bleeding off charges from the resist and preventing charge buildup in the resist layer, which otherwise deflects the e-beam and creates placement errors.

In this same study [29], the conductivity of polyaniline was varied in order to determine the level that is actually required to eliminate resist charging. The conductivity was adjusted by changing the pH of the aqueous acid dopant solution [36, 54]. It was found that a conductivity greater than 10^{-4} S/cm^2 is required to prevent pattern displacement in the interlayer structure. The level of conductivity needed for charge dissipation depends on the actual resist structure configuration.

In this first evaluation of polyaniline as a charge dissipator in resist systems, the polymer was processed in two steps. The base form of the polymer, which is generally the more soluble form of polyaniline, was first spin-applied onto a surface. The sample was then converted to the conducting form by dipping it into an aqueous acid solution. The doping reaction takes several

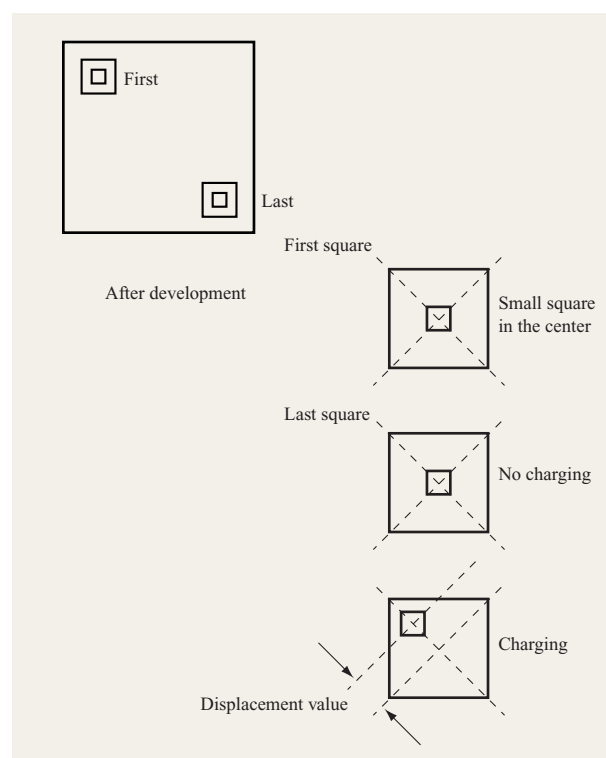


Figure 5

Evaluation of e-beam discharge test results. The pattern displacement is that observed from the first to the last (400th) square written. (From [29].)

hours to ensure the diffusion of the dopant into the bulk of the film. This process is not desirable because it increases the number of steps and prolongs the exposure of substrates to acid solutions, posing contamination, reliability, and corrosion concerns.

In a subsequent study [55], a simplified one-step process for applying the polyaniline to resist systems was reported. A method of inducing the doping *in situ* in the polymer was developed, thereby eliminating the need for external acid solutions. This was accomplished by incorporating salts in the polymer which would decompose upon irradiation or thermal treatment to generate the active dopant species, i.e., a protonic acid, *in situ* in the material [55–57]. These salts were of two types—onium and amine triflate salts.

Onium salts such as triarylsulfonium and diaryliodonium salts are a class of materials which decompose upon exposure to ultraviolet radiation or to an e-beam to generate a protonic acid [58, 59]. They are discussed further in the subsection on conducting resists. A conductivity of 0.1 S/cm^2 was attained when a polyaniline base film containing an onium salt was irradiated [56].

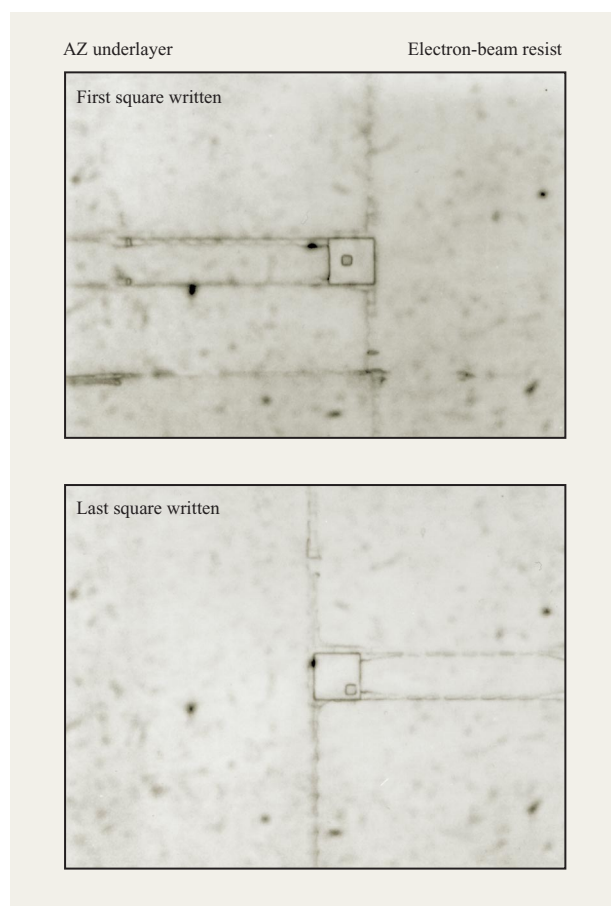
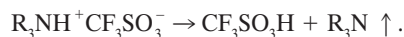


Figure 6

Image placement results for a control resist system having no conducting layer. A displacement greater than $5\text{ }\mu\text{m}$ is measured across a 5-mm chip. (From [29].)

Amine triflate salts thermally unblock to generate the free triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) with the volatilization of the corresponding amine, as shown below [60, 61]:



The temperature at which the salts decompose and doping occurs can be tuned by the nature of the amine group. The less volatile or more basic the amine is, the greater the temperature required to decompose the salt. Thus, this method offers great latitude in allowing the polyaniline process to be made compatible with the resist process. Triethylammonium triflate, for example, decomposes at 90°C . When a polyaniline film containing this salt was baked for five minutes at this temperature, a conductivity of 1 S/cm^2 was reported, comparable to that measured with aqueous acid solutions [55, 57].

In the studies described thus far, the polyaniline is incorporated below the imaging resist. In these systems,

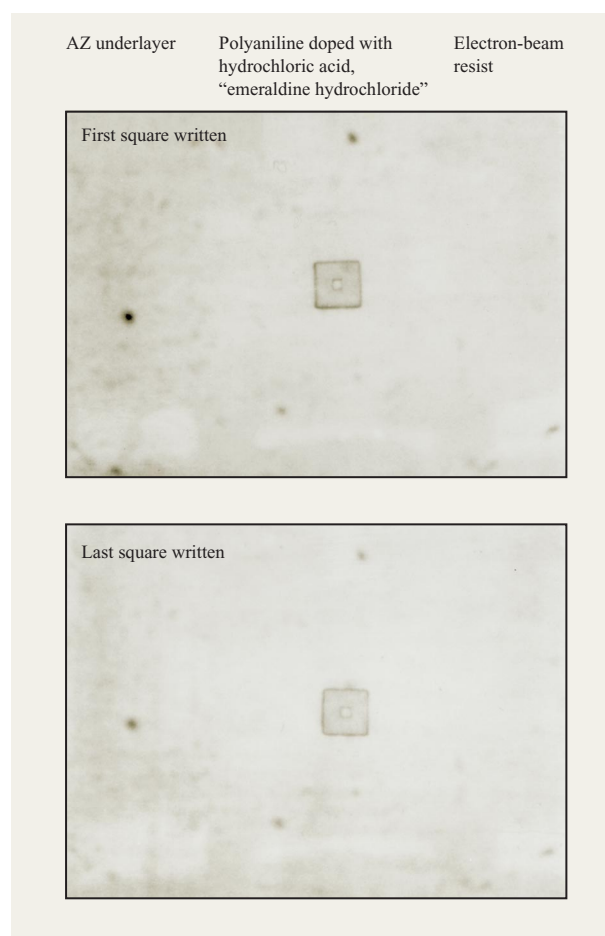


Figure 7

Image placement results for a resist system containing a polyaniline interlayer. Zero pattern displacement is observed. (From [29].)

once the resist is exposed and developed, the polyaniline remains in the open areas, as shown in **Figure 8(a)**. To transfer the pattern to the underlying substrate, the exposed polyaniline is removed by reactive ion etching (RIE) with oxygen [4, 15, 29, 62].

Although the method of utilizing polyaniline below the resist works quite well, an easier and more optimum approach is to apply the conducting layer on top of the resist and to have the conductor removed simultaneously with the development of the resist. This configuration and process are depicted in **Figure 8(b)**. Because the conductor in this case is applied directly on the resist, it must meet certain requirements. First, the solvent used to coat the conducting polymer must not dissolve the resist nor induce any interfacial problems. Thus, polar solvents such as N-methyl pyrrolidinone (NMP), which is commonly used to process polyaniline, are not acceptable because they would dissolve most commonly used resists.

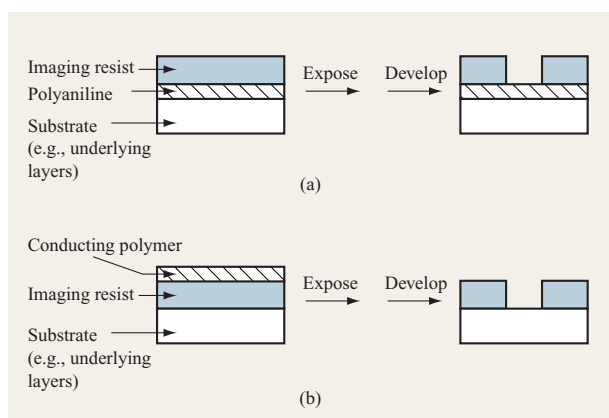


Figure 8

(a) Multilayer resist structure incorporating polyaniline as an interlayer. After resist is exposed and developed, polyaniline remains in open areas. Etching of polyaniline is required to transfer image. (b) Multilayer resist structure in which the conducting polymer is applied as a topcoat discharge layer. The conducting polymer is removed during resist develop.

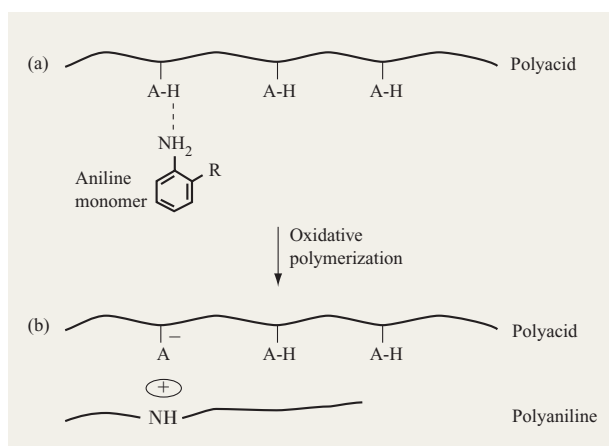


Figure 9

Template-guided polymerization of water-soluble polyanilines (PanAquas): (a) aniline monomer is complexed to a polyacid template. (b) Complex is oxidatively polymerized in a controlled fashion.

The conducting polymer must not degrade the lithographic performance of the resist. It should not introduce any contamination. In addition, it should be cleanly removed, and if possible, during the development of the resist. Since most resists currently used in the industry are developed in aqueous systems, the conducting polymer must be soluble in these systems.

In recent years, a number of polyaniline derivatives have been developed which are soluble in the conducting

form [46, 48, 50]. A few of these derivatives are soluble in water [41–43, 51, 63–67]. One method of introducing water solubility has been the incorporation of sulfonate groups onto the polymer backbone. This has been accomplished by several routes. One process involved the sulfonation of the polyaniline base by treating the polymer with fuming sulfuric acid [41, 64]. This results in a sulfonic-acid ring-substituted derivative that is alkaline-soluble, but only upon conversion to the nonconducting, sulfonate salt form. A second method of introducing sulfonate groups was to deprotonate a polyaniline base and react with a sultone, i.e., 1,3 propanesultone [65, 66]. This gives rise to an N-substituted polyaniline derivative which is water-soluble. Another route involved the polymerization of sulfonated aniline monomers such as the sodium salt of diphenylaminesulphonic acid [42, 43]. At IBM, a family of water-soluble polyanilines [51, 67] referred to as PanAquas were introduced which are highly soluble in the conducting form in neutral water. They are fabricated in a one-step, straightforward synthesis involving a template-guided polymerization (**Figure 9**). In this reaction, the aniline monomer is first complexed to a polymeric acid. Once the complex is formed, the aniline is polymerized in a controlled fashion, allowing the growing polyaniline chain to wrap around the polyacid chain and thereby preventing the formation of an interpenetrating network. As a result, the polyaniline/polyacid blend which is isolated directly in the conducting form is water-soluble. A number of different derivatives can be created by this method through variations in the nature of the aniline monomer (i.e., through variations in R in Figure 9) and in the nature of the polyacid. Conductivity for these polymers is of the order of 10^{-2} to 10^{-4} S/cm².

The PanAquas provide a simple and effective solution to charging during e-beam lithography [67]. In particular, the unsubstituted derivative in which $\text{R}=\text{H}$ in Figure 9 was spin-applied onto the surface of a number of common resists used in the industry such as novolacs, acrylates, and chemically amplified systems [4]; it was compatible with the resists and did not affect their performance.

A 200-nm layer was quite effective at eliminating charging of the resist, as is seen in **Figure 10**, which compares a pattern written with no topcoat (a) to one that contained the PanAqua topcoat (b). As can be seen, severe image distortion is observed in (a), whereas a well-defined image is observed in (b). The PanAqua can be cleanly removed during the alkaline development of the resist [67].

In a recent study published by Etec Systems [25], a number of conductors were evaluated as charge dissipators for phase-shift mask (PSM) [4, 68, 69] e-beam registered writing. Several materials were studied in parallel, and their ability to improve the overlay accuracy of the two

lithography levels in the PSM process was compared [25]. The first-level pattern was a reference consisting of butting crosses which was written onto a resist-coated chrome/quartz plate. After the pattern was delineated and etched into the chrome, the second registered level pattern was written using a novolac resist and a charge dissipator including aluminum, chrome, indium–tin oxide, and the PanAqua. The overlay accuracy between the two levels was determined from the butting overlay of crosses between the reference level and the registered level—an overlay accuracy of less than $0.07\text{ }\mu\text{m}$ ($\pm 3\sigma$) was attained. From these results, it was concluded that all of the conductors tested provided excellent charge dissipation. Also, PanAqua provided the simplest solution because it was a spin-apply process that did not involve an evaporative deposition, as was necessary with the other materials.

Another conducting polymer that has been of interest for charge dissipation in e-beam lithography is the water-soluble, self-doped polythiophenes such as the sulfonated derivatives which have the general chemical structure shown in **Structure 2** [28, 70–72]. The one disadvantage with these materials compared to the polyanilines is that they are prepared by a cumbersome synthetic procedure, because the sulfonic-acid-substituted thiophene monomers do not directly polymerize. A typical synthesis for the poly(3-(2-ethanesulfonic acid))thiophene, for example, begins with the monomer, 2-(3-thienyl)ethanol, and is converted in five synthetic steps to the methyl-2-(3-thienyl)-ethanesulfonate [71], which is then polymerized. The polymethylester is in turn converted to the polysodium salt, from which the self-doped acid version is then obtained by ion exchange chromatography [71].

Recently, this polythiophene derivative was evaluated as a topcoat discharge layer that was applied to a typical novolac resist [28]. The polymer was found to be very effective at eliminating resist charging. In another study [73], charging was eliminated during e-beam writing by applying a water-soluble polythiophene derivative, referred to as ESPACER**, to a chemically amplified resist. In this system, the ESPACER was removed by a water wash prior to the development of the resist.

As the microelectronics industry continues to move toward increased circuit density, with a concomitant decrease in device geometries, higher precision in e-beam writing will be required. Any surface charge on the resist can reduce the precision of the writing. Thus, discharge layers will probably be necessary in the future. The water-soluble conducting polymers have been shown to offer not only an effective approach to eliminating resist charging, but also much simpler processing than do currently used materials such as metal coatings.

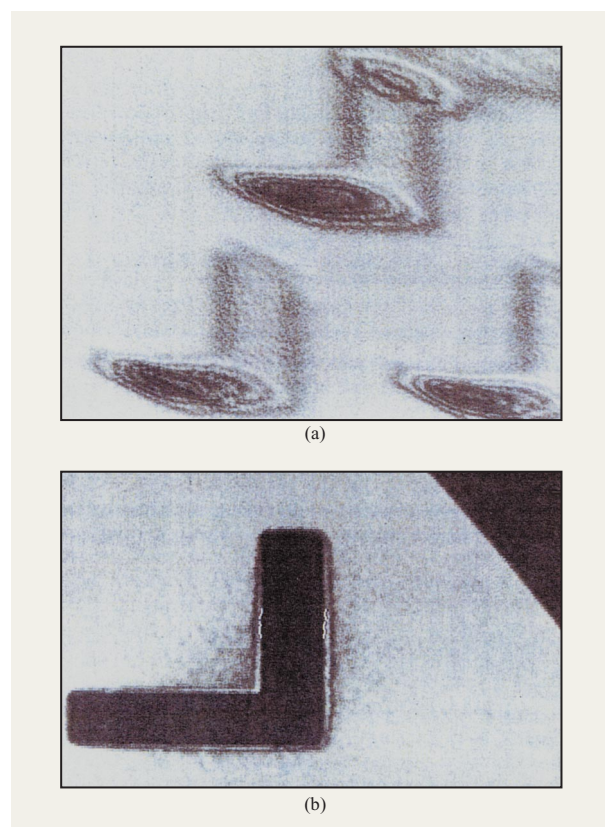
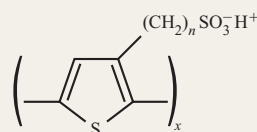


Figure 10

Photomicrographs comparing resist patterns: (a) Resist imaged with no discharge layer; image distortion observed. (b) Resist imaged with a water-soluble polyaniline topcoat; no image distortion observed. (From [67].)



Structure 2

Water-soluble polythiophene derivative.

Charge dissipators for scanning electron microscopic metrology

Scanning electron microscopy (SEM) offers increased resolution capability in comparison to optical microscopy and is a commonplace technique for inspection and dimensional measurements (metrology) of circuits [74–76]. Measurements are made, for example, on actual device wafers or on high-resolution masks. Charging of the

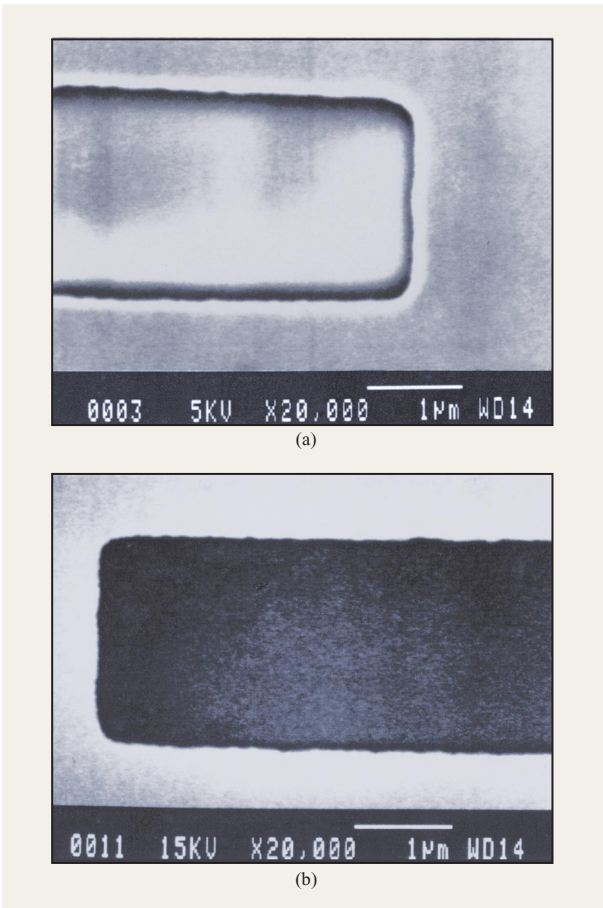


Figure 11

(a) Metrology of an uncoated mask with SEM. Pronounced charging observed. (b) Metrology of a polyaniline-coated mask with SEM. No charging observed. (From [77].)

sample during SEM makes accurate metrology difficult because the electron beam can be deflected as an electric field builds up on the sample. Even a very small beam deflection around a feature can move the beam one or two pixel points and introduce substantial error into measurements of the critical dimensions.

One method to partially alleviate the SEM charging problem is to make measurements at accelerating voltages lower than 2 keV [74–76]. However, at such voltages the resolution of the measurements is sacrificed. As device geometries continue to shrink, low-voltage SEM may not be an effective tool for metrology. Another method to prevent charging is to coat the sample with a conducting metal such as gold. Although this permits high-resolution metrology, it is a destructive process because the metal cannot be totally removed from the surface of the substrate, thereby preventing further use of the device or mask.

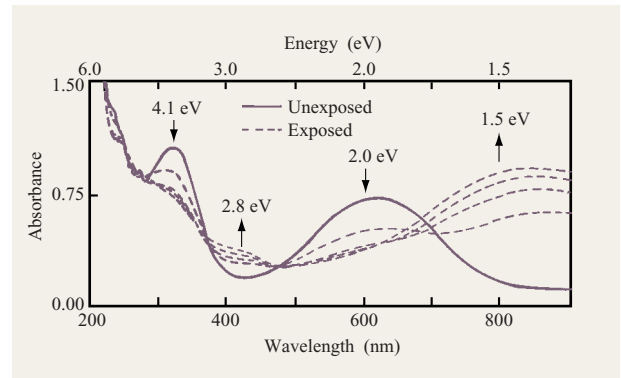


Figure 12

Optical absorption spectra for the polyaniline/onium salt before (solid curve) and after (dashed curves) different doses of exposure. The same film was used for all scans. (From [56].)

Conducting polymers that can be spin-applied onto the sample and subsequently cleanly removed provide a nondestructive process which would allow high-resolution SEM metrology. In a recent report [77], a 150-nm-thick layer of polyaniline was coated onto the surface of an optical mask. The coated mask and an uncoated control mask were then inspected with SEM. Pronounced charging was observed at 5 kV on the uncoated mask [Figure 11(a)], whereas no charging was observed on the polyaniline-coated mask even at 15 kV [Figure 11(b)]. After the measurements, the polyaniline was removed from the surface of the mask by rinsing with a solvent.

Conducting resists

In the applications discussed in the previous sections, the conducting polymers function as added charge-dissipative layers which are subsequently removed. The resists which are used to delineate the circuitry patterns are insulators. If the resists were conducting, there would be no need for an additional dissipative layer—only one polymer coating would be necessary. A sensitive, high-resolution, water-developable conducting resist would offer significant process simplification.

A great deal of activity has been directed toward the development of conducting resists. The first report [29] of such a polymer was based on the radiation-induced doping of the unsubstituted polyaniline base with onium salts. These salts have been shown to decompose readily upon irradiation to generate protonic acids [58, 59]. They were previously used to photochemically dope polyacetylene [78] and polypyrrole [79]. In these systems, because the polymers are insoluble, the polymer films are impregnated with the salts. In the polyaniline case, the polymer and the onium salt (e.g., triphenylsulfonium hexafluoroantimonate)

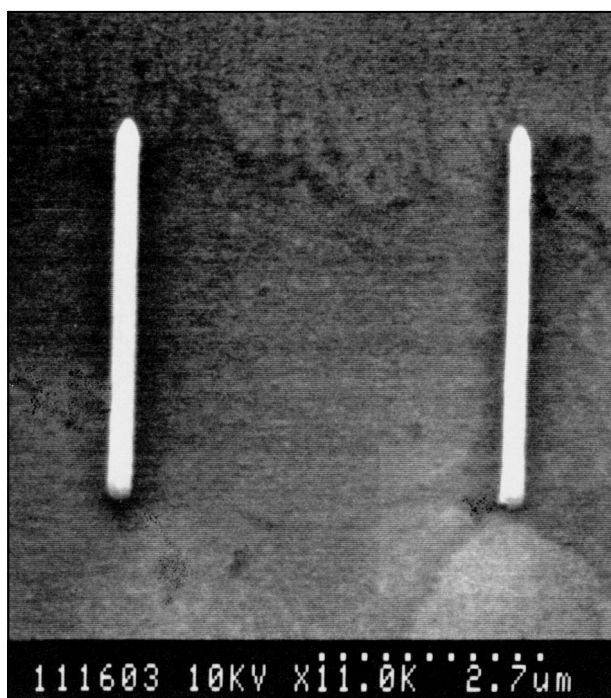


Figure 13

Conducting polyaniline lines ($0.25\ \mu\text{m}$ wide) patterned with e-beam irradiation. (From [55].)

are dissolved in NMP and processed into a film. Upon exposure of the film to ultraviolet radiation or to an e-beam, the generated acid dopes the polymer. **Figure 12** depicts the optical changes that are observed in the polyaniline/onium salt film upon ultraviolet irradiation [56]. Polaron absorptions [80, 81] characteristic of the conducting form of polyaniline emerge; conductivity is of the order of $0.1\ \text{S}/\text{cm}^2$ [56]. Since the doped polymer is no longer soluble, a solubility difference is created between exposed and unexposed regions. Thus, a negative conducting resist developed in a mixture of NMP/diglyme was attained [29, 55–57]. Using an e-beam, $0.25\text{-}\mu\text{m}$ -wide conducting lines in a $0.25\text{-}\mu\text{m}$ -thick film (**Figure 13**) were written with this system. The sensitivity of the resist was of the order of $100\ \mu\text{C}/\text{cm}^2$ to the e-beam and $300\ \text{mJ}/\text{cm}^2$ to deep UV.

In a later study [83], a similar method was used to pattern the methyl-substituted polyaniline, poly-o-toluidine. This material is a more soluble derivative than the unsubstituted parent polymer used in the previous study and thus allows a broader range of solvents to be utilized. A non-ionic nitrobenzyl sulfonate ester was used as the photoacid generator. The polyaniline derivative was mixed in methyl ethyl ketone with the acid generator and exposed to ultraviolet radiation. Upon irradiation, a

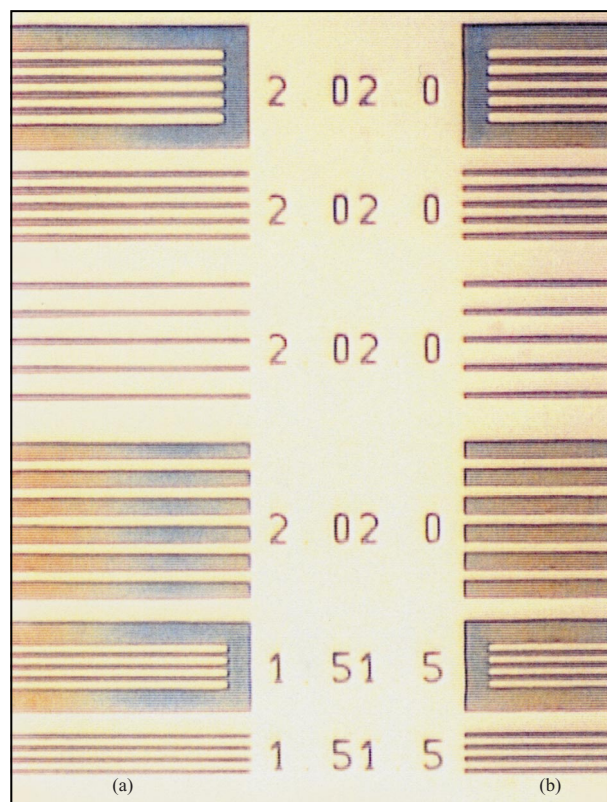


Figure 14

Features (a) $1.5\ \mu\text{m}$ and (b) $2.0\ \mu\text{m}$ wide, delineated with the poly-o-toluidine system. (Courtesy of G. Venugopal, Motorola Corporation [82].)

conductivity of the order of $10^{-7}\ \text{S}/\text{cm}^2$ was attained. The conductivity was subsequently increased to $10^{-3}\ \text{S}/\text{cm}^2$ by externally doping the photodoped samples with HCl acid. Although a large increase in conductivity was not observed upon irradiation, the photoinduced doping did create a large enough solubility difference to differentiate doped and undoped regions. **Figure 14** depicts 1.5- and $2.0\text{-}\mu\text{m}$ features delineated with deep UV. The resist was not very sensitive, since a dose of $1500\ \text{mJ}/\text{cm}^2$ was required.

A water-developable, negative conducting resist based on the PanAquas was more recently reported [51, 67]. Cross-linkable functionality was incorporated into the polyaniline backbone so that, upon e-beam irradiation, the polyaniline cross-linked and became water-insoluble. Images of conducting lines $1.0\ \mu\text{m}$ wide in a $0.75\text{-}\mu\text{m}$ -thick film, which were patterned with an e-beam at a dose of $200\ \mu\text{C}/\text{cm}^2$, were then developed with water (**Figure 15**). Lines $250\ \text{nm}$ wide were also delineated. This resist is quite promising because it is a water-developable conducting resist, but its lithographic performance

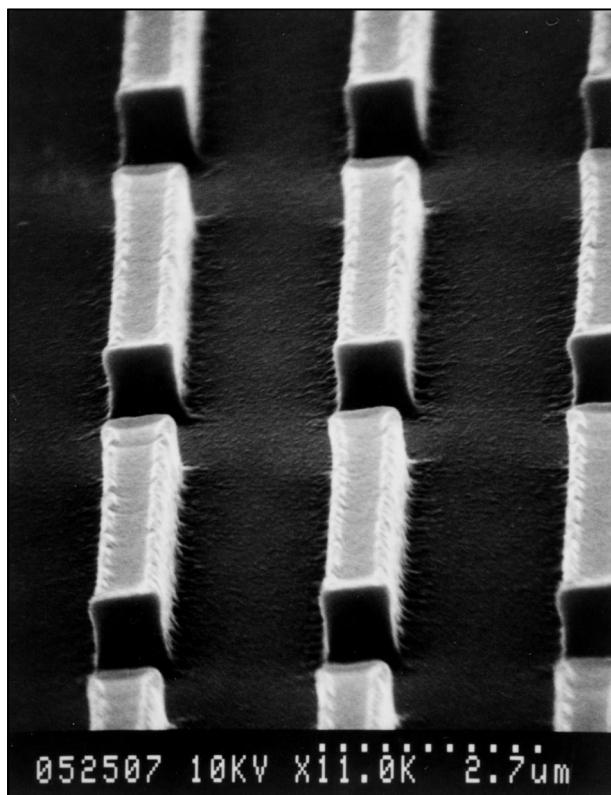


Figure 15

Conducting polyaniline lines (1.0 μm wide) in a 0.75- μm -thick film patterned with e-beam irradiation. Image developed in water. (From [67].)

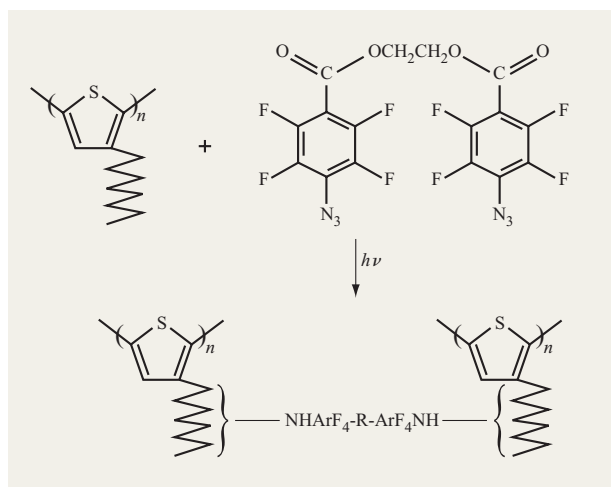


Figure 16

Schematic depicting radiation-induced cross-linking of poly(3-octylthiophene) using the 1,2-bis(4-azido-2,3,5,6-tetrafluorobenzoate) cross-linker. (From [83].)

requires significant improvement. Much higher sensitivity and resolution are required.

Conducting resists have also been reported with polythiophenes. One of the first examples [83, 84] was based on poly(3-octylthiophene) (P3OT). The nondoped form of the polymer was combined with a cross-linking reagent, ethylene 1,2-bis(4-azido-2,3,5,6-tetrafluorobenzoate). Upon exposure to deep UV, cross-linking through the octyl side chain was induced, as depicted in **Figure 16**. The authors proposed that this occurred by CH insertion by a triplet nitrene intermediate into the octyl side chain. This two-step process involved hydrogen abstraction followed by radical combination. This system cross-linked upon e-beam irradiation as well. In addition, the polymer without the cross-linker was also noted to cross-link with e-beam irradiation. Negative images of non-doped P3OT were attained using xylene as the developer. This resist has relatively high sensitivity; an e-beam dose of 30 $\mu\text{C}/\text{cm}^2$ was reported, and 0.2- μm features were delineated.

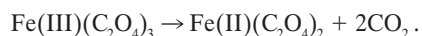
Figure 17 is a micrograph depicting a wire pattern structure of cross-linked P3OT written with an e-beam [83, 84]. This resist exhibits good lithographic performance, but the images are attained on the nondoped polymer, and thus the process of forming a conducting resist requires more than one step. The authors did find that doping could be induced after the images were developed by dipping the patterned film into an FeCl_3 solution. Conductivity of 5 S/cm^2 was measured on the doped wire pattern depicted in **Figure 17**. A similar system based on poly(3-hexylthiophene) was subsequently reported [85].

An extension of the substituted thiophene work involved the incorporation of methacrylate functionality onto the thiophene backbone [86, 87]. Methacrylates are widely known to undergo free radical polymerizations. Poly(3-2-(methacryloyloxyethyl)thiophene) and copolymers with other substituted thiophenes with the basic structure depicted as **Structure 3** were synthesized.

The polymers undergo cross-linking through the methacrylate side chains upon irradiation. Negative images developed in organic solvents were obtained, and 3- μm -wide lines in a 75-nm-thick film were written. The resist had good sensitivity (14 mJ/cm^2) at a wavelength of 313 nm [87]. In this system, as in the previous polythiophene examples, the imaged patterns must subsequently be doped to make the patterns conducting.

A completely different approach to patterning conducting polymers involves the use of photosensitive oxidants [88, 89]. In this process, a photosensitive oxidant is mixed with a host polymer such as poly(vinyl chloride), poly(vinyl alcohol), or polycarbonate, and the composite is applied to a substrate. Upon irradiation of the film, the oxidant in the exposed regions is made inactive, whereas

in the unexposed regions the oxidant can still induce polymerization of appropriate monomers. After exposure, the latent image is exposed to a monomer such as pyrrole either in solution or in the vapor state. Polymerization occurs only in the nonexposed areas where the oxidant is still active. In this fashion, patterns consisting of conducting composite materials are delineated. Some photosensitive oxidants include Fe(III) salts such as iron trichloride or ferrioxalate. Upon exposure, Fe(III) is converted to Fe(II), which does not induce oxidative polymerization [88, 89]:



Methods of imaging conducting polymers either directly in the conducting form or in the precursor, nondoped form have been developed. These methods are appropriate in applications in which the conducting polymer must be patterned to a certain geometry. However, for these imageable conducting polymer methods to be utilized in lithography, the lithographic performance of the conducting resists must be improved, because they are currently not competitive with conventional resists [4, 12, 17] in terms of resolution, sensitivity, and contrast. Further work in this area is required to bring the conducting polymer-based resists closer in performance to conventional resists.

Metallization

In microelectronics, the term *metallization* generally refers to a patterned film of conducting material deposited on a substrate to form interconnections between electronic components [2, 7]. Over the last few years, conducting polymers have been demonstrated to provide a new route to metallization, particularly in printed circuit board (PCB) technology [90–94]. In general, conducting polymers can be utilized for both electrolytic and electroless metallization. The conducting polymers that have been of interest in this area include polyaniline [90], polypyrrole [91–94], and polythiophene [93].

The complexity of PCBs [95–97] vary from single-sided boards, where circuitry is found on only one side, to double-sided boards, to boards comprising multiple layers of circuitry. The degree of complexity depends on the specific interconnection requirements for a given product. Connections between the two sides of a board and layer-to-layer connections are made with copper-plated through-holes (PTHs) [95–97], allowing greater circuit density because they provide crossover capability. A circuit crosses over another by simply entering a PTH, continuing on the other side, and so on.

The through-holes are drilled into the laminate substrate and are then copper-plated. **Figure 18** depicts two common metallization schemes for PCBs [95–98]. In one method [Figure 18(a)], a conducting “strike”

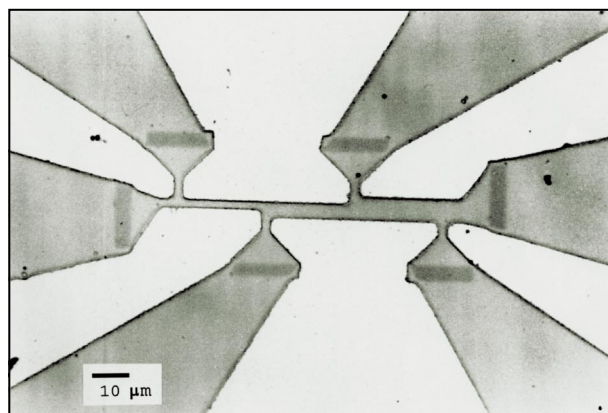
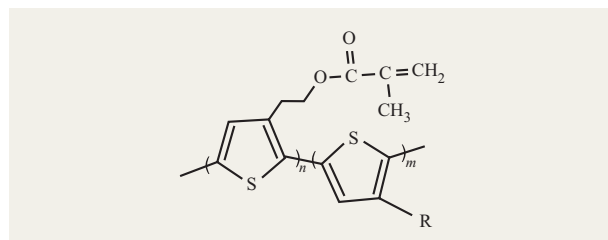


Figure 17

Micrograph depicting a cross-linked poly(3-octylthiophene) wire pattern delineated with e-beam lithography. (Courtesy of J. Keana and M. Wybourne, University of Oregon [83].)



Structure 3

Polythiophene-methacrylate structure.

layer (generally a thin layer of copper) is deposited by electroless plating. This copper layer renders the surface sufficiently conducting to allow a thicker copper layer to be electrolytically deposited in selected regions defined by a photoresist process. In an alternate method [Figure 18(b)], an all-electroless process is used. The current processes have certain disadvantages. Electroless deposition requires the use of expensive noble-metal salts, such as PdCl₂, as seeds. The salts are applied to the PCB surface followed by reduction of the noble metal to the zero-valent state. The zero-valent noble-metal particles are the active sites for heterogeneous copper reduction in electroless plating.

Electroless baths are generally unstable and require close monitoring. The baths can fluctuate between being too stable, resulting in PTH voids, and being too active, resulting in homogeneous decomposition of the bath. Formaldehyde, the most commonly used reducing agent in electroless baths, is toxic and poses environmental concerns.

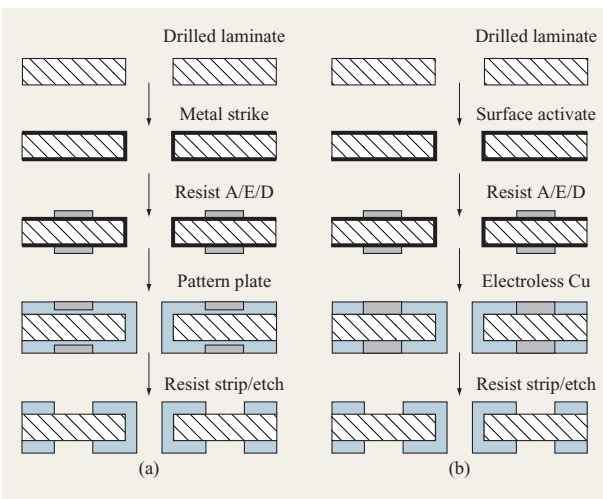


Figure 18

Metallization schemes for PCBs: (a) Initial conducting strike layer deposited followed by electrolytic pattern plate-up. (b) All-electroless process. In each scheme, the pattern is defined by a photoresist. (A/E/D is apply, expose, develop.) (Courtesy of A. Viehbeck, IBM Thomas J. Watson Research Center.)

An alternative to current methods is the use of a conducting polymer as an electrode for direct electrolytic metallization of copper. At IBM, polyaniline was used in this application [90]. Because of its solubility, the polymer was deposited directly onto a PCB by a dip-coating process. In one study [90], a PCB was coated with a 1- μm -thick layer of polyaniline applied from an aqueous acetic acid solution. The polyaniline-coated board was electrolytically copper-plated. As shown in **Figure 19(a)**, the copper started to plate on the hole wall from the two contact sides and grew inward until the copper front met at the center of the hole wall. As the plating process continued, a thicker, uniform copper coating was deposited on the polyaniline surface [**Figure 19(b)**]. Today, as a result of the many soluble polyaniline derivatives that have been developed, a variety of solvents including water can be used to apply the polymer.

Another method of applying conducting polymers to direct electrolytic metallization of circuit boards was introduced by Blasberg Oberflächentechnik [91]. They reported that polypyrrole [91] and poly-3,4-ethylenedioxythiophene [93] were deposited onto the surface of a circuit board using an *in situ* polymerization route (**Figure 20**). After the substrate is selectively coated with an oxidant solution, the monomer (pyrrole or 3,4-ethylenedioxythiophene) is introduced, followed by acid-induced *in situ* polymerization of the monomer. The

conducting polymer-coated board can then be directly electrolytically copper-plated. The polypyrrole process, referred to as DMS-2, was first marketed by Blasberg Oberflächentechnik in 1990 [91]. The polythiophene process, DMS-E, has also since been marketed [93, 99]. It has been reported that both of these processes are currently in full-scale production in more than forty companies worldwide [93, 99].

Another variation to the use of conducting polymers for metallization was based on spontaneous noble-metal deposition induced by a conducting polymer [90]. It was found that polyaniline can spontaneously reduce noble-metal ions such as Pd^{2+} and Ag^+ to their zero-valent state upon immersion of the polymer in an aqueous solution of the corresponding metal salt. Thin films of Pd^0 and Ag^0

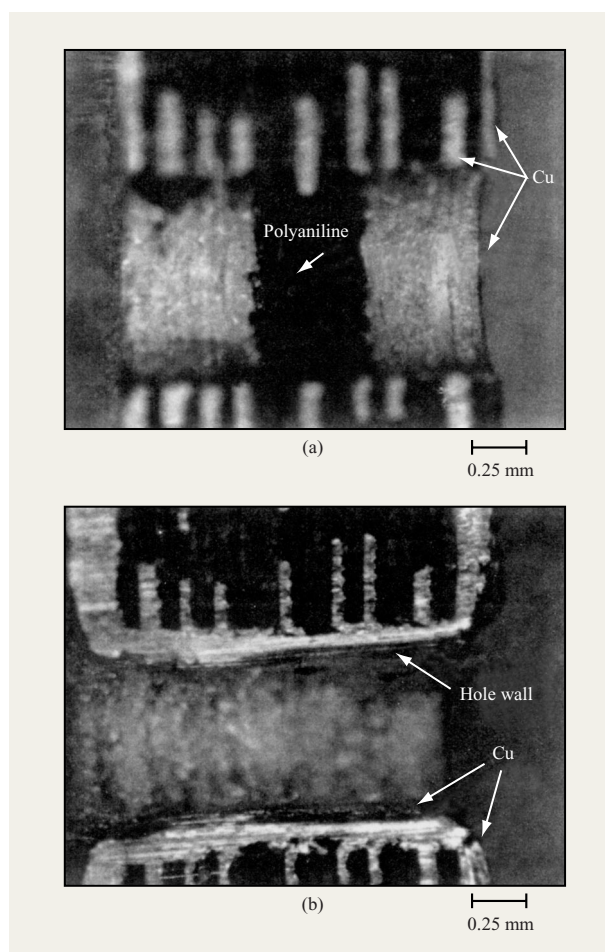


Figure 19

(a) Micrograph depicting a cross section of a polyaniline-coated through-hole on which electrolytic copper deposition has begun. The copper plates from the two contact sides and continues inward on the polyaniline-coated hole wall. (b) Polyaniline through-hole that has a continuous copper deposit. (From [90].)

deposit on the polymer surface without an external reducing agent [90]. While this approach does not preclude the use of a precious metal, it does eliminate the need for subsequent activation of the metal. The Pd⁰-coated polyaniline can be used for subsequent electrolytic as well as electroless metallization.

It should be pointed out that the use of imageable conducting polymers described in the previous section is applicable to metallization. A conducting polymer could be applied to the circuit board surface and directly imaged, thereby eliminating an additional photoresist process. Electroplating could then occur selectively on the patterned conducting polymer.

Corrosion protection of metals

Metals such as copper (Cu) and silver (Ag) are widely used in microelectronics for wiring and EMI shielding. Although both are noble metals, they readily corrode in a variety of ambients [100–103]. In oxygen-saturated water, Ag and Cu dissolve with a measurable corrosion rate of about 1×10^{-7} and 1×10^{-5} A/cm², respectively, or 0.002 and 0.2 nm/min, as determined from the potentiodynamic polarization curves shown in **Figure 21** [104–106]. With increased anodic potential, metal dissolution increases rapidly by exceeding 10^{-1} A/cm² corresponding to catastrophic metal removal at a rate of at least 35 nm/s [104–106]. In the presence of an applied potential and humidity, not an uncommon situation for devices in operation, these metals dissolve from the more electrically positive metallic part of the device and plate at the more negative part as dendrites [100–106], which can cause shorts. Dendrite formation between two unprotected copper lines is depicted in **Figure 22**. In addition, with increasing line density and decreasing dimensions, ion accumulation alone without dendrite formation can destroy the designed electrical performance of the product. Inhibitors such as benzotriazole (BTA) provide excellent corrosion protection for Cu and Ag metals [100–103]. However, these azole-type inhibitors do not provide protection at high temperature (i.e., in a soldering application), nor do they protect against an applied potential [102, 103]. Therefore, new materials are needed to protect Ag and Cu against corrosion and dissolution, particularly at high temperatures and in the presence of an applied potential.

For more than a decade, the use of polyaniline for corrosion protection of metals, such as stainless steel, has been investigated. In the first study, by Berry [107], polyaniline was electrochemically deposited on ferritic stainless steels and was found to provide anodic protection that significantly reduced corrosion rates in acid solutions. Numerous studies since then have

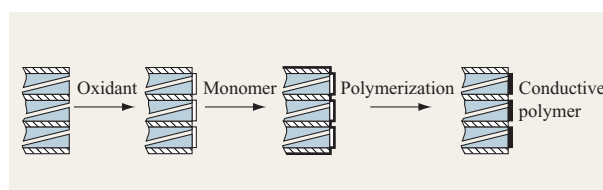


Figure 20

Blasberg Oberflächentechnik process for *in situ* polymerization of a conducting polymer onto a circuit board. (Courtesy of D. Bruce, Uyemura International Corporation.)

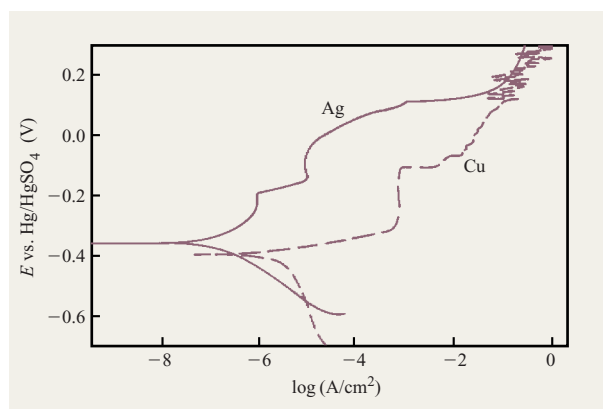


Figure 21

Potentiodynamic polarization curves for unprotected Ag and Cu measured in a droplet of water. (From [106].)

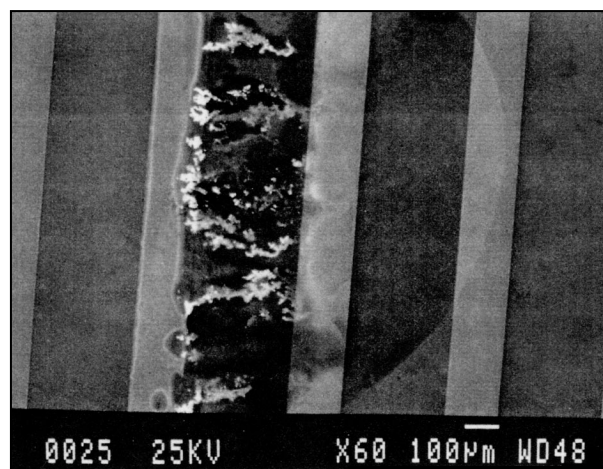


Figure 22

Dendrite formation between two unprotected Cu lines after a water droplet is placed across adjacent metal lines and a bias of 5 V is applied between the lines.

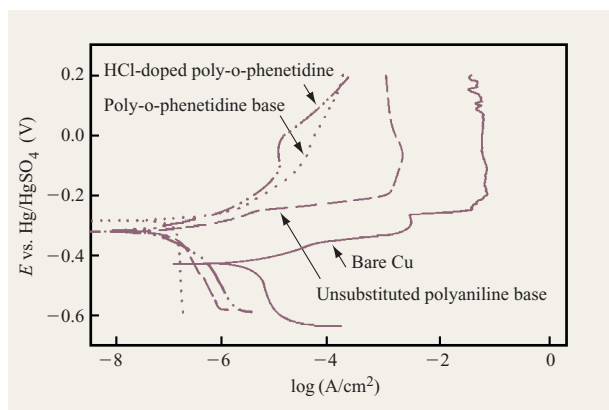


Figure 23

Potentiodynamic polarization curves in a droplet of water for bare Cu, and for Cu coated with poly-o-phenetidine base, HCl-doped poly-o-phenetidine, and with unsubstituted polyaniline base. (From [106].)

confirmed the corrosion-protective properties of polyanilines¹ [104–106, 108–112].

Non-electrochemical methods of applying polyaniline have been demonstrated¹ [104–106, 108–112]. In one recent study, dispersions based on doped polyaniline (Versicon**) passivated mild steel, stainless steel, and copper [110].

The use of polyaniline to protect Cu and Ag at high temperature and under an applied potential, which is of interest to the microelectronics industry, was extensively studied by Brusic et al. [104–106]. A number of soluble polyanilines were evaluated in both the nondoped and doped forms. These materials were tested by two procedures which were designed to closely simulate conditions to which these metals may be exposed during actual use in an electronic product (as in, for example, a PCB). In most cases, the corrosive environment would vary depending on the relative humidity, i.e., the amount of adsorbed water on the surface. One procedure utilizes a three-electrode electrochemical cell using a water droplet as an electrolyte [113]. This procedure makes use of a sample working electrode which is the coated metal masked with plating tape to expose a 0.32-cm² area, a Pt mesh counter electrode, a mercurous sulfate reference electrode, and a filter paper disk to separate the electrodes. The corrosion potential is monitored for 15 minutes, and the polarization resistance is measured by scanning the potential ± 20 mV from the corrosion potential. The potentiodynamic polarization curve is measured from 0.25 V cathodic of the corrosion potential. The corrosion rate is evaluated by extrapolation of the

cathodic and anodic currents to the corrosion potential. In this study [105], the metal dissolution rates at high anodic potentials were closely monitored. In a second procedure, patterned metal lines were tested for ease of dendrite formation by placing a water droplet across adjacent metal lines with an applied potential between the lines.

Soluble poly-o-phenetidine, particularly in the nondoped form, which is highly soluble in a variety of organic solvents, was found to provide excellent protection for Cu and Ag and was superior to the unsubstituted polyaniline base [104–106]. Homogeneous and adherent films 184, 339, and 477 nm thick were spin-applied onto Ag and Cu surfaces from an NMP or γ -butyrolactone solution and evaluated. Even the thinnest film provided a perfect barrier to oxygen, since the electrochemical data indicates no current dependence attributable to oxygen reduction, as seen in **Figure 23**. Oxygen reduction (generally the main cause of Cu and Ag corrosion) is completely inhibited. The cathodic current of about 2×10 A/cm² is independent of film thickness, type of metal, and ambient atmosphere. The current is diffusion-limited and is probably caused by reduction of the polymer backbone. The anodic current metal dissolution is greatly reduced by a factor which increases with film thickness. The protection is substantial, especially at high potentials, where Cu dissolution is about four orders of magnitude lower than that measured on bare Cu. Similar results were observed with Ag [104–106].

The corrosion protection offered by the doped version of poly-o-phenetidine is similar to that of the nondoped form except for the measurement of the oxygen reduction rate. Since this form is conducting, it allows the passage of electrons which are needed for oxygen reduction but prevents the passage of metallic ions. At anodic potentials, the protection provided by the film is still excellent.

In terms of dendrite formation, it was found that poly-o-phenetidine provided exceptional protection [104–106]. Bare Cu and Ag were observed to form dendrites within seconds of an applied potential, as evidenced by shorting of the lines. BTA was found to be ineffective, since BTA-protected metal lines formed dendrites within seconds as well. Metal lines that were coated with poly-o-phenetidine base did not form dendrites, even after 30 minutes of applied potential of 5 V. The coated lines were also tested at elevated temperature (220°C for 30 minutes); dendrites were not formed under these conditions. A temperature/humidity study was performed in which the poly-o-phenetidine-coated metal was stored for 1000 hr at 85°C and 80% relative humidity; again, no dendrites were observed. In a more drastic test, a 5-V potential was applied to the coated metal while at 85°C and at 80% relative humidity for 1000 hr. No failure was observed under these conditions as well.

¹A. G. MacDiarmid, International Conference on Synthetic Metals, Kyoto, Japan, 1986, personal communication.

The poly-o-phenetidine provides excellent corrosion protection for Cu and Ag at elevated temperatures as well as under an applied potential. The superior protection offered by this polyaniline derivative may stem from its excellent coverage and adhesion to the metal surface. It has good solubility and forms very uniform films. In addition, the ethoxy group can complex with the metal and enhance its adhesion characteristics. Indeed, peel test results show adhesion strength in excess of 60 g/mm [106]. Generally, values greater than 50 g/mm for polymer-to-metal adhesion are considered to be excellent.

Electrostatic discharge protection for electronic components

Electrostatic charge (ESC) and electrostatic discharge (ESD) constitute a serious and expensive problem for many industries—in particular for microelectronics [114–119]. It has been estimated that \$15 billion a year is attributed by the U.S. electronics industry to ESD damage alone [114, 115].

Electrostatic charge can accumulate to thousands of volts. The static charge can attract airborne particles, as is often observed on cathode ray tubes (CRTs). This becomes a significant contamination concern if particles are attracted to critical surfaces such as device wafers. The accumulated charge will eventually discharge in the form of a “lightning bolt” which can destroy devices on ICs [114–119]. **Figure 24** depicts an example in which a discharge created a “punch-through” effect that exposes lower layers of a circuit. As IC circuit density continues to increase and the area and thickness of the active device elements continue to shrink, device sensitivity to the destructive effects of ESD will continue to increase.

To protect devices against ESC and ESD, conducting materials are used extensively in clean rooms during their manufacture. In addition, conductors are incorporated into plastic packages which are used to transport sensitive electronic components such as chips, modules, and PCBs. The materials currently used include ionic conductors, carbon- or metal-filled resins, and, in certain cases, metal coatings [119]. These materials do not offer the ideal solution to ESD protection. The use of ionic conductors, although an inexpensive approach, has significant drawbacks. These materials exhibit very low surface conductivity (10^{-9} to 10^{-11} S/□) and thus are not dissipative. The conductivity is humidity-dependent, since water is needed as an electrolyte for ionic conduction. In addition, since ionic conductors can readily be removed by water, any washing of structural parts containing these materials is precluded. The use of ionic conductors is not a reliable method for ESD protection. Electrical conductors, on the other hand, are stable systems with conductivities that are not humidity-dependent. However, the use of these materials is a more expensive alternative.

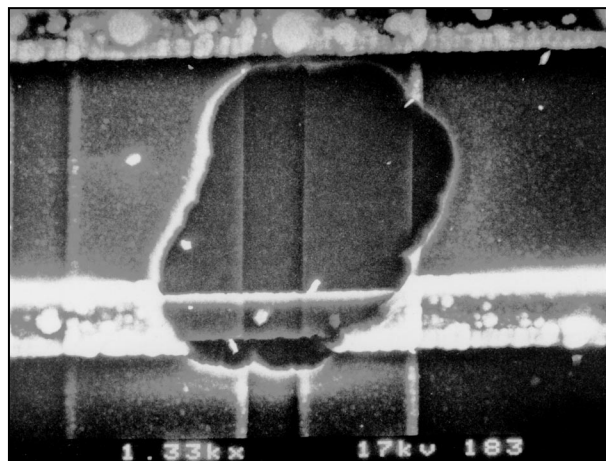


Figure 24

Example of ESD damage to an IC. A “punch-through” effect has occurred which exposes lower layers of a circuit.

Carbon-filled systems pose contamination concerns because of sloughing of the carbon particles. In addition, relatively high loading levels are required to attain a given level of conductivity. Such high loading can degrade the mechanical/physical properties of the host polymer. With high loadings, recyclability of the plastic carriers becomes more difficult.

Conducting polymers offer a new alternative for ESD protection, with numerous advantages over current materials. The conductivity of such polymers can be tuned, can easily meet the high end of the dissipative range, and is stable in comparison to ionic conductors. By appropriate design of the conducting polymer, contamination concerns can be eliminated. In addition, conducting polymers can offer a high degree of transparency. Polyaniline, polypyrrole, and, more recently, polythiophene have been the predominant conducting polymers of interest for ESD protection. These polymers have been used as fillers in a number of host resins. In addition, coating formulations have been developed which can be applied directly onto plastic surfaces.

Pyrrole has been polymerized *in situ* onto the surface of textile fabrics [120, 121]. A number of polypyrrole-coated fabrics, such as Contex**, have been produced by Milliken Research Corporation [120, 121].

Polyaniline in the form of a dispersible powder, Versicon, has been blended with a number of thermoplastic and thermoset resins, resulting in blends which have excellent ESD properties [122–126]. Soluble polyanilines have also been blended with appropriate polymers [127, 128]. In the latter systems, very low loadings have been reported to be necessary to reach a certain level of conductivity [127, 128].

Of particular interest for ESD protection of electronic component packages are coating formulations. The coatings can be applied directly onto already fabricated packages by spray-coating, or they can be applied onto plastic sheets which are subsequently thermoformed into a package. A number of coatings based on conducting polymers have been developed and are currently commercial. One type of coating is based on dispersions of Versicon [124–126, 129, 130]. Such coatings have been produced by Americhem [124–126, 129]. Coatings based on soluble polyanilines have also been produced. One such system is a curable, water-based coating reported by IBM [51, 130]. An aqueous coating based on poly(3,4-ethylenedioxythiophene)/polystyrenesulfonic acid blend has recently been developed [131, 132]. This material is reported to exhibit effective antistatic properties. The formulations based on soluble conducting polymers have the advantage that they pose no contamination concerns due to particles. This is of particular importance for microelectronics, where actual devices are in contact with the conducting carriers. Any particle sloughing would contaminate the devices. Some of the conducting polymer coating formulations described above are currently in commercial use for ESD protection.

Future applications of conducting polymers

Other potential applications of conducting polymers in microelectronics exist aside from those discussed above. Conducting polymers can in principle be considered as candidates for interconnection technology. The use of conducting polymers for wiring has been widely speculated upon since the emergence of these materials in the late 1970s. For such an application, copper-like conductivity is necessary. Unfortunately, polyacetylene is the only conducting polymer that currently exhibits such conductivity, and its environmental instability and lack of processability preclude its use. A dramatic enhancement of the conductivity of some of the more processable and environmentally stable polymers is required before they can be realistically considered as viable conductors for interconnection technology.

The use of conducting polymers in devices [133–138] is another area that may provide new technology in the future for IC fabrication and flat-panel displays. This is currently an active area of research, and is discussed elsewhere in this issue [139].

Conclusions

Conducting polymers have a broad range of applications in microelectronics. In the area of lithography, they have been shown to provide an effective, simple spin-apply process for charge dissipation, in particular for e-beam lithography and for SEM metrology. A number of resists based on conducting polymers have been developed.

However, the lithographic performance of these systems is not currently at a stage that can compete with conventional resists. Significant improvements in resist resolution, contrast, and sensitivity are required. Conducting polymers are currently used for metallization of plated through-holes for printed circuit board technology in a number of companies worldwide. Conducting-polymer-based coatings have been developed that offer excellent ESD protection and numerous advantages over materials in current use. A number of the coating formulations are either already commercial or in the process of being rendered commercial. Corrosion protection of metals such as silver and copper using conducting polymers has also been shown to be quite promising.

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Figures 4–7, 10–13, 15, 19, 21, and 23 were reprinted with permission from [13].

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