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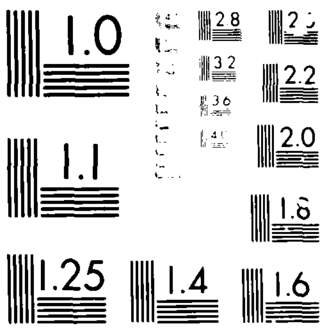
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Improved Adhesion of Thin Conformal Films to Metal Surfaces

by

Kevin R. Stewart and George M. Whitesides

Herman P. Godfried and Isaac F. Silvera

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Improved Adhesion of Thin Conformal Organic films to Metal Surfaces

Kevin R. Stewart and George M. Whitesides

Department of Chemistry, Harvard University, Cambridge, MA 02138

and

Herman P. Godfried and Isaac F. Silvera

Department of Physics, Harvard University, Cambridge, MA 02138

Abstract. A technique is described for attaching thin, conformal, pin-hole free electrically insulating polyethylene films to flat gold surfaces (previously modified by adsorption of a monolayer of an organic disulfide) by plasma polymerization. These polyethylene films are tough enough to support the attachment of gold electrodes.

In recent years there has been a growing activity in the preparation of thin film devices and components on surfaces, not only for microelectronic fabrication, but also in various areas of experimental physics and chemistry. In our own case we were faced with the requirement of depositing a thin film heater and capacitor plates on a high thermal conductivity substrate for use at temperatures below 1°Kelvin. We chose copper as the substrate material. It was desirable that the components not only be electrically insulated from the substrate,[1] but also in very good thermal contact, for removal of heat, suggesting the use of a very thin insulating layer. An initial attempt to precoat the copper with a few microns thick silicon oxide layer by vapor deposition failed the electrical integrity requirement due to pinholes in the insulating layer. This technique is particularly unsuitable if conformal[2] coatings are required on surfaces which are not flat, due to shadowing of the deposition source.

A useful technique, which can potentially provide pinhole free conformal coatings, is flow discharge polymerization, sometimes referred to as plasma polymerization.[3-5] During a plasma polymerization, an electrical discharge taking place in an organic or inorganic gas, or mixture of gases, results in the formation of a thin polymer film on the surfaces exposed to the discharge. This technique originally seemed a solution to the problem of controlled fabrication of thin organic dielectric films. Initial hopes of rapid application of these films as dielectrics did not, however, materialize, because their characteristics degradated on aging and on exposure to moisture. These problems continue to inhibit the technological applications of these films.[6] We undertook investigations designed to improve the adhesion of plasma polymerized thin organic films to metal surfaces.

Initial investigations involved the coating of cleaned copper surfaces with plasma polymerized ehtylene (PPE) in a Hummer X sputter coater.[7] The copper pieces were rectangles cut from copper sheet which had been cleaned with soap and water, distilled water, acetone and trichloroethylene, then etched with an argon plasma in the sputter coater immediately prior to use. The synthesis of the PPE thin films was accomplished by placing the substrate pieces on the lower horizontal electrode of the sputter coater. A target aluminum electrode was placed parallel to the lower electrode at a separation of 55 mm. The chamber was repeatedly evacuated and refilled with argon to remove contaminating gases, then evacuated and refilled three times with ethylene.[8] An AC plasma (60 Hz) was created in the chamber of the sputter coater while maintaining an ethylene pressure of 100 mtorr. After 5 min the plasma was turned off, and the chamber was evacuated and slowly brought to atmospheric pressure by bleeding in argon. The resulting films were dark grey and insoluble in organic solvents and water. The advancing contact angle of distilled water on the film surface was $\theta_a = 90\text{-}93°$, in good agreement with the reported values for polyethylene surfaces.[9] Qualitative test of the adhesion of the film to the copper surface, carried out by a peel test[10] with Scotch tape (3M-810), revealed that the films adhered well to the rough surface of the copper.

We next applied this technique to coating the surface of hand-polished copper disks.[11] The PPE films did not adhere to these polished surfaces. The films appeared intact until exposed to the room atmosphere, at which time they lost adhesion and flaked. This process was accelerated by breathing on the surface. These effects were independent of the type of copper that was used. We attempted to change the surface character of these polished copper disks, prior to coating with PPE, by treatment with aqueous chromium trioxide, aqueous sodium formate, dilute nitric acid, by electropolishing the disks in a 68% aqueous phosphoric acid solution, and by sputter coating the surface with thin layers of gold, silver and platinum, but found that all gave equally poor adhesion of the PPE thin film to the substrate. Mechanically roughening these surfaces produced the same film qualities (good adhesion) as was observed previously on the stock sheet copper surfaces. We therefore concluded that adhesion of the PPE film to the rough copper surfaces occured mainly through sticking to surface asperities of size larger than about 3 μm.[12]

Having failed in simple attempts to change the surface character of the copper to obtain better physisorption of the PPE thin film, we turned our attention to modification of the surface using a designed adhesion promoter. Nuzzo and Allara[13] demonstrated that long hydrocarbon chain disulfides reacted with clean gold surfaces and gave chemisorbed organic monolayers in which the alkyl chains were fully extended with their longest axis largely perpendicular to the gold surface. These monolayers were stable at ambient conditions.[13] To make use of this monolayer technology in modifying the interphase between our copper substrate and the PPE thin films, we synthesized di-ω-docosenyldisulfide **1** (hereafter called the disulfide) by the reactions shown in Figure 1.[14] This long chain disulfide had a carbon-carbon double bond in the terminal position of its C_{22} hydrocarbon chains. We hoped this double bond would bond covalently to the growing polyethylene chains produced in the glow discharge.

In our experiments the polished copper disks were first sputter coated with a thin film of gold and then soaked in a dilute solution of the disulfide in hexadecane for 12 hours. The disks were removed from the disulfide solution and carefully washed with hexane; their surface was oleophobic to hexane.[15] The disks were treated with the ethylene plasma. Plasma polymerization resulted in assembly of a composite thin film represented schematically in Figure 2. These films are deep blue in color and do not fail in the Scotch tape adhesion T test. They also survive cycling between room temperature and 77 °K (immersing in liquid nitrogen), and are unaffected by drops of acetone and water on their surface. Examination of the films with an optical microscope (100x) and with SEM (10000x) indicates that the films are pinhole free at that scale, and that they conform to surface irregularities in the metal stock. Examination of the films with ESCA (XPS) reveals a significant peak due to oxygen (either from reaction of radical centers on the film with dioxygen upon exposure to air at the completion of

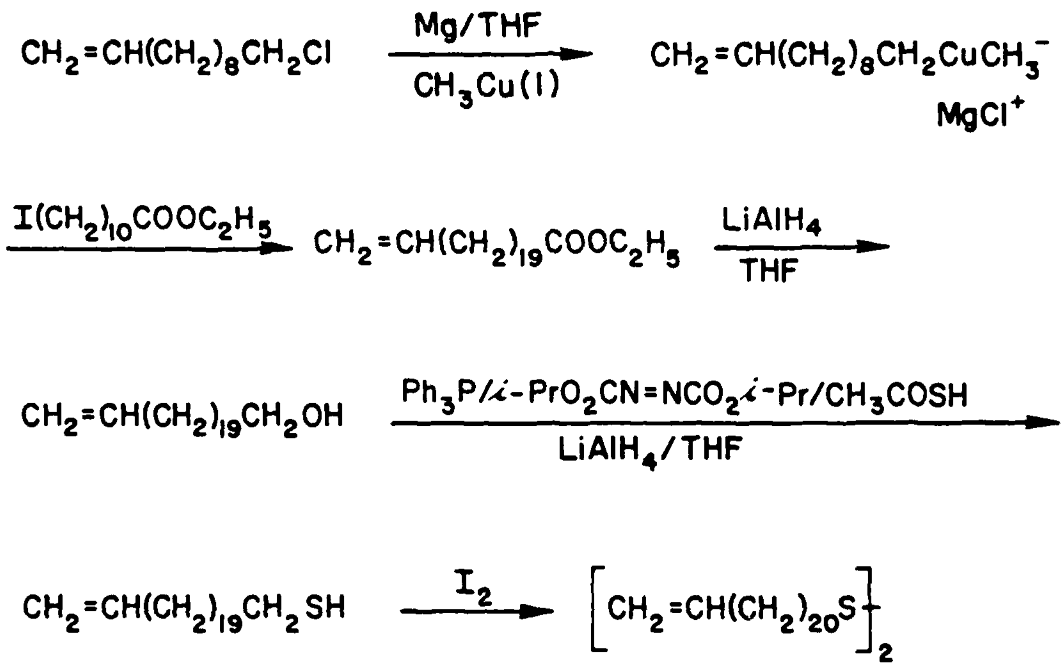

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Figure 1. Scheme of reactions for the synthesis of di-ω-docosenyldisulfide.

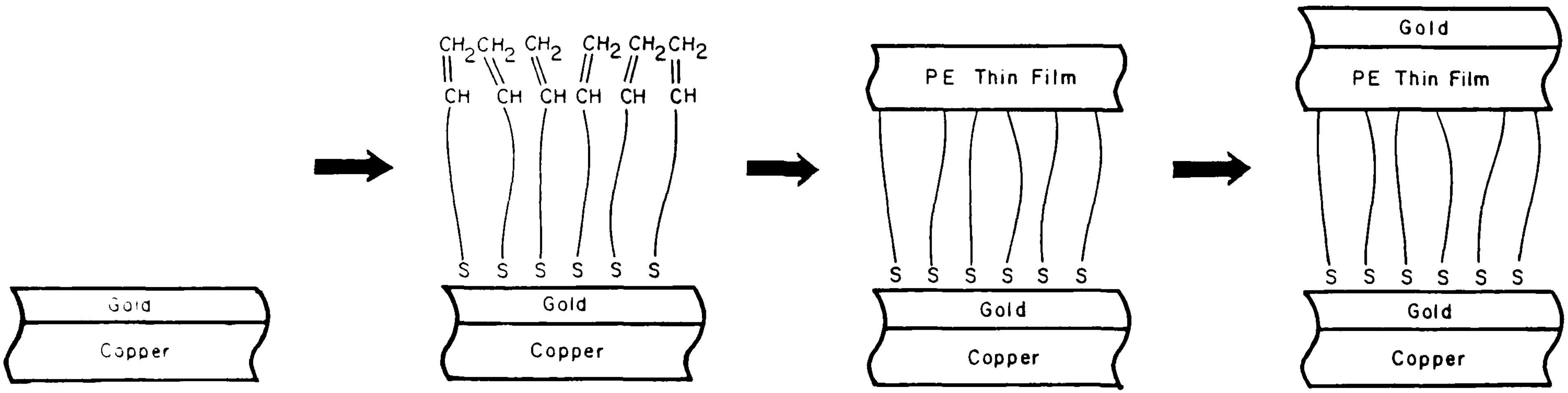

Figure 2. Schematic diagram of the surface in the various steps used for fabricating an insulating PE conformal coating.

the plasma polymerization process,[1,6,16] or from incorporation of oxygen from dioxygen or water, into the films during plasma deposition present as impurities in the vapor); no other element (other than carbon) is evident. The ESCA spectrum of these films shows no gold or sulfur, supporting the microscopic evidence that the thin films are free of macroscopic pinholes.

As a final step in fabrication of the thin film, we placed a gold electrode on its surface to test its electrical conductivity. The electrode was sputter coated onto the surface through a mask.[17] The resistivity of the film was carried out by attaching leads to the gold electrode region of the surface and to the copper disk: the resistance was greater than 1 megohm. These films have retained their properties on exposure to air for periods of over one year.

In conclusion, we have shown the adhesion of plasma polymerized polyethylene (PPE) thin films to a gold surface can be dramatically improved by coupling the synthesis of the PPE thin film with the prior assembly of an organic monolayer chemisorbed to the metal surface. These thin film assemblies have good physical characteristics and are stable to the ambient environment for long intervals. We believe this method should be applicable to other systems with appropriate modifications.

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11 Disks were made from electrolytic tough pitch copper (Copper Development Association Alloy Designation #110) or from oxygen free high conductivity copper (CDA #101). The disks were handpolished on a felt covered polishing wheel using aluminum oxide (Al_2O_3) abrasive powder. The surfaces obtained in this manner had a surface roughness of approximately

0.15 μ, were hydrophilic and pink in color. Some disks showed "deep" scratches (10-100 μ deep) from machining. These were left in the surface to test the conformity of our coatings to surface irregularities. After polishing, the disks were cleaned ultrasonically with water and methanol to remove any weakly bound abrasive particles and then the disks were stored in methanol to prevent oxidation and keep the surface as clean as possible.

12 Surface roughness after electropolishing was ~3 μ as measured by optical microscopy.

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Captions

Figure 1. Scheme of reactions for the syntheis of di-ω-docosenyldisulfide.

Figure 2. Schematic diagram of the surface in the various steps used for fabricating an insulating PPE conformal coating.

APPENDIX

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