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Patterning Ultrathin Polymethylene Films: Applications as a Resist in Electrochemical Growth of Conducting Patterns

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Micrometer scale patterns of continuous and inert polymethylene films were prepared on gold surface, using self-assembled thiolate monolayer as the primary resist. The polymethylene film served as a secondary resist to block electrochemical activity of underlying gold surface. Application of this pattern to fabricate micrometer-scale conducting circuits was demonstrated.

Keywords: self-assembled monolayer; patterned films; polymethylene; polyaniline

INTRODUCTION

Formation of microfeatures of conducting materials such as conducting polymers and metal wires is an important part of microelectronics. A number of techniques have been developed for this purpose, such as photolithography, e-beam writing, laser writing, and surface-template deposition. Self-assembled monolayers (SAMs)[1] of alkanethiol, although as thin as ~2 nm, have evolved to be a new type of resist that can block reactions that can otherwise occur on a gold electrode surface. On the other hand, a specific reaction can be carried out at a modified surface, if an appropriate functional group is incorporated to the monolayer. [2] In combination with the micro-

contact printing (μCP) method, [3] microfeatures can be readily made. However, thiolate-based monolayers suffer from disadvantages of chemical or electrochemical instabilities, besides structural defects that almost always present within the monolayers.[4] We report here the use of ultrathin polymethylene films[5] as the alternative resist in forming patterned microcircuits of conducting polymer or metal on gold surface.

EXPERIMENTAL SECTION

Materials. Diazomethane was freshly prepared in ether and the concentration was titrated with benzoic acid solution. The gold substrates were prepared on polished silicon wafers as described earlier.[5]

Monolayer patterning and polymethylene patterning. Micro-contact printing technique[3] using PDMS stamp was adopted for patterning the surface. The thiol monolayer was imprinted first, followed by dipping into an ethereal solution of diazomethane for various amounts of time to achieve different polymer thickness. The thickness of the polymethylene film was checked by ellipsometry, AFM or profilometer.

Electrodeposition of the second component. The electrochemical polymerization of aniline was carried out by potential cycling between -0.2V and 0.85V vs Ag/AgCl in a medium containing 0.1 M aniline, 0.85 M H_2SO_4 and 0.25 M $NaHSO_4$.[6] Electrodeposition of silver metal was carried out by electrolysis at a constant potential of 0.2 mV in the presence of 1 mM $AgClO_4$ and 0.1 M $NaClO_4$ aqueous solution.

Characterization. The set-ups for characterization, such as cyclic voltammetry, reflection absorption IR spectroscopy, atomic force microscopy and scanning electron microscopy have been described previously.[6]

RESULTS AND DISCUSSION

Micrometer-scale patterned polymethylene film was prepared on a gold surface patterned with a self-assembled monolayer as the resist.

Depend on the structure of the monolayer-forming thiols and the reaction time, polymethylene films with various thickness can selectively grow on bare gold surface while growth on the monolayer-covered surface was greatly retarded. Figure 1 shows the AFM micrographs of two representative samples with different thickness of polymethylene grown on hexadecanethiol-patterned Au surface. The polymer growth was previously shown to start from the grain boundary regions and spread to form a continuous film as it gets thicker.[5] The left one shows a polymethylene film of ~80 Å. Although the surface is smooth and appear continuous. Repeated potential cycling in the presence of aniline solution gave current response, indicating there are still defects where the electron transfer between the gold and electroactive species in the solution existed. The right one shows a film of ~300 Å. The polymethylene film was still very smooth and a total blockage of gold was confirmed by testing with redox probe or repeated potential cycling in aniline solution. When a much thicker film is grown (>1000 Å), the roughness increases substantially on both polymer and the monolayer-covered areas.

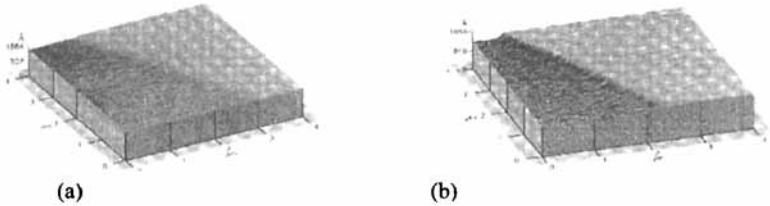
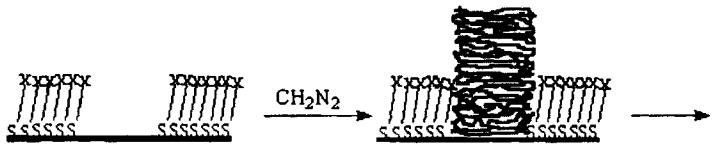
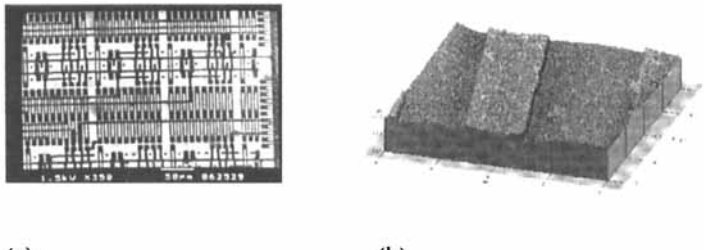


Figure 1. AFM micrographs (4μx4μ) of (a) ~80 Å and (b) ~300 Å polymethylene films grown on monolayer-patterned gold..

The stability of the film was shown by the aquaregia etching of the monolayer/gold area. The 300 Å polymethylene-covered area, together with the gold underneath, survived while the thiol/Au area was all etched. Repeated potential cycling did not remove the film. However, it does dissolve in refluxing *p*-xylene. The polymer film served not only as the resist to prevent etching or barrier for electrochemical reactivity of the gold surface, but also served as a retainer to prevent lateral growth found sometimes in using monolayer as resist. The strategy is outlined in the following scheme.



Depending on the "composite" pattern to be prepared, monolayers with different terminal X group can be chosen as the primary resist. Thus to prepare a patterned polyaniline film, a dimer aniline-terminated monolayer (X= $C_6H_5NHC_6H_5NH$) was imprinted by micro contact printing first. Electropolymerization following the polymethylene film formation was carried out in the presence of aniline to give the "two dimensional" composite polymethylene/polyaniline pattern. In this case, the dimer aniline moieties served as the initiation sites in the polyaniline formation.[6] By controlling the number of cycles, polyaniline films of different thickness were formed in the "trenches" defined by the walls of polymethylene. Overflow of polyaniline and thus loss of pattern were observed after extensive cycling. Figure 2 shows the SEM and AFM images of one of such a pattern, which contain ~300 Å of polymethylene and ~100 Å of polyaniline. A sharp edge with a line resolution of ~0.1 micrometer was obtained.



(a) (b)

FIGURE 2. (a) SEM and (b) AFM micrographs of polyaniline(~100Å)/polymethylene(~300Å) pattern.

Similar strategies can be used to prepare polymethylene/polythiophene and polymethylene/polypyrrole patterns starting with appropriate polymerizable monomer attached at the terminal of the monolayer.[7] For the deposition of metal pattern, an acetylene-terminated monolayer ($HC{\equiv}C(CH_2)_{15}SH$) was used as the primary resist. The terminal acetylene group can be readily converted to silver acetylide. The silver ions served as the nucleation sites in the electrodeposition of silver metal. Figure 4 shows the SEM image of the polymethylene/Ag composite pattern. Some silver crystals are observed on a smoothly deposited silver. AFM imaging further confirms the observation.

FIGURE 3. SEM micrograph of a silver/polymethylene pattern prepared by electrodeposition.

In conclusion, a smooth, micrometer-scaled, patterned polymethylene film can be formed on gold surface using appropriate monolayer as the primary resist. Although defect spots in the monolayer can result into some scattered growth of polymethylene, these will be buried and rendered negligible in later deposition. The inert and stable polymethylene film, in the thickness range of several hundred angstroms, serves as a better resist in the electrochemical preparation of another component of the interdigitated and patterned material, such as polyaniline circuits or metal wires. Efforts in searching for other non-polar and insulating polymers as the template material are in progress.

Acknowledgements

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[7] Detailed results will be published elsewhere.