

be treated as a general purpose method for the low-cost synthesis of doped metal oxides, having many applications as photocatalysts. The synthesized photocatalyst powder may be used in the form of discs of appropriate dimensions, as employed here, or alternatively may also be spin-coated on suitable substrates to have thin films of photocatalysts. It is also hoped that by regulating the experimental conditions of reaction eqs (1)–(3), probably the nanoparticles of metal-oxides can be generated quite economically. Work in this direction is in progress, and results will be communicated soon.

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Selective growth of polypyrrole on ω -pyrrolyl undecanethiol monolayer-patterned gold surface using micro-contact printing technique

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Micrometre-sized conducting polypyrrole pattern was generated on gold surface using microcontact printing (μ -CP) technique. ω -pyrrolyl undecanethiol was used as ink to print on gold surface with an elastomeric stamp. The patterned gold surface was then exposed to diazomethane solution in which the monomer acted as a resist for the selective growth of polymethylene on unmodified gold surface. The pyrrole terminal monolayer-patterned surface functioned as a monolayer for the chemical polymerization of pyrrole and the resulting formation of conducting polypyrrole pattern with submicron dimensions. The structural features of the patterned surface can be determined by optical microscopy, AFM and scanning electron micrograph.

THE self-assembling behaviour¹ of long-chain alkanethiol is of immense interest in recent days because of its widespread applications in academics and industry. Alkanethiols can form a well organized and ordered monolayer

assembly when exposed into coinage metal surfaces. The self-assembled monolayers (SAMs) are a robust, spontaneous organization of molecules and act as a resist against oxidative etching. The monolayer controls many properties of the surface such as wettability, adhesion, etc.^{1–3}. The SAMs act as ultrathin resists in lithographic techniques. Fabrication involving SAMs is cheap when compared with conventional lithographic techniques. There are a wide variety of techniques that have been used for generating patterns with micron-dimension including UV-photolithography^{4–7}, electron-beam writing^{8–10}, micro-writing¹¹, dip-pen writing¹², atom lithography¹³, micromachining (using an STM tip¹⁴ or sharp stylus¹⁵), micromoulding in capillaries (MIMIC)¹⁶ and microcontact printing (μ -CP)^{17–20}. These techniques can be used in the development of nanodevices in sensor and drug-screening applications. Among these techniques, the microcontact printing technique is considered to be simple, easy and it can be used in the ordinary wet chemical laboratory.

The stamp is formed by curing polydimethylsiloxane (PDMS) on a master whose surface has been patterned with a complimentary relief structure using photolithography, or from a commercially available relief structure such as diffraction grating¹⁷. The PDMS stamp is wetted with ink, wherein molecules of the ink are transferred from the stamp to the surface of the gold substrate that is in contact with the stamp by hand-pressing for a short exposure (~ 2 s). Microcontact printing is being used for making patterns with alkanethiol as a resist on Au, Ag and Cu²¹. Similarly, silanes and phosphate-terminal long-

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chain molecules can form a well-organized resist for the generation of pattern using the above technique^{22,23}. For the generation of micron-dimension patterns, various etching agents²⁴ have been proposed depending upon the oxidation potential and the nature of bonding to etch the unmodified metal surfaces. In general, long-chain monolayer assembly ($\geq C16$) can be used for generating patterns with submicron dimensions, which can be used in the electronic industry.

Nowadays, the conducting-polymer pattern is generated either by chemical or electrochemical polymerization methods. Rozsnyai and Wrighton²⁵ have used the SAM technique to generate the pattern of conducting-polymers such as polypyrrole, poly(3-methylthiophene) and polyaniline, through selective electropolymerization of the respective monomers onto the photochemically patterned SAMs on gold, wherein the monolayer served to promote the polymer deposition. Gorman *et al.*²⁶ have used short-chain alkanethiol monolayer to grow conducting polypyrrole patterns in which the monolayer retarded the charge transfer process from species in solution to the electrode surface. Huang *et al.*²⁷ have reported the selective deposition of conducting polymers on hydroxyl-terminated surface with printed monolayers of alkylsiloxanes as template, using chemical polymerization method. These patterned structures of conducting-polymers were conductive and hence used in electronic display devices. A detailed investigation has been carried out on polymer growth on various functionalized monolayer-patterned substrates. It was found that amine-terminal monolayer effectively blocked the electrochemical polymerization of aniline and pyrrole due to electrostatic repulsion between the charged monolayer and the monomer species²⁸. A detailed report has been given on the growth mechanism of polymethylene thin-film on gold surface²⁹. We have suggested a new polymeric resist, polymethylene (PM) for the effective blocking of polymer growth³⁰, since the monolayer may not block the electrochemical reaction due to defects in the monolayer assembly or due to the presence of grain boundaries in the gold substrates³¹.

In the present investigation, we are interested to use monomer-functionalized alkanethiol pattern as a resist as well as a monomer for polymer growth. The polymerization reaction was carried out by using the chemical method. The thickness of the polymer pattern is controlled by the exposure time and monomer concentration.

All chemicals were purchased from commercial sources. Pyrrole and Bu_4NPF_6 were obtained from Aldrich, USA. Anthraquinone 2-sulphonic acid sodium salt monohydrate, sulphosalicylic acid dihydrate and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from Merck, Germany. The ω -(N-pyrrolyl) undecanethiol (PyC_{11}SH) was obtained from our previous work³⁰.

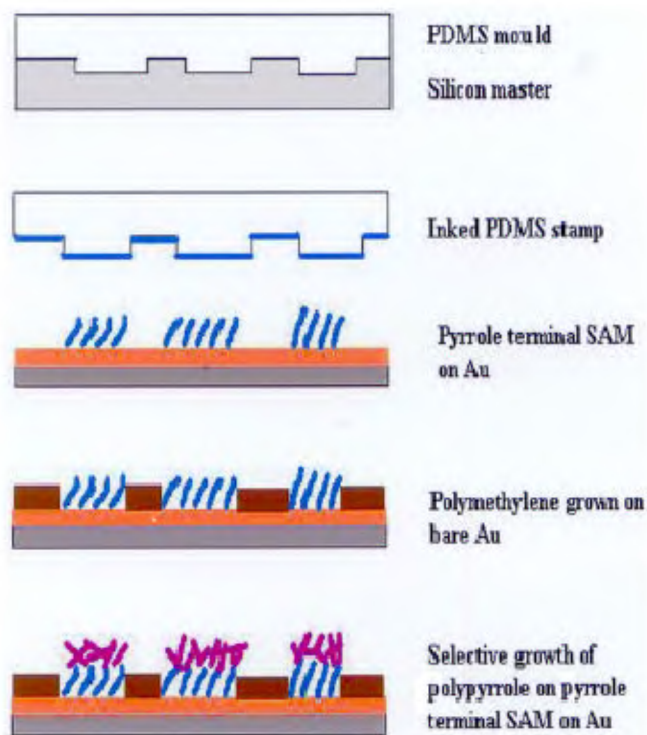
Chromium (5 nm) and gold (100 nm) were evaporated in sequence at 0.15 nm/s and 0.4 nm/s respectively, onto 2-inch silicon wafers in a diffusion-pumped chamber with

a base pressure of 7×10^{-6} torr. The gold-coated wafers were cut into small pieces and used for the patterning work.

The fabrication of an elastomeric PDMS stamp was described in more detail in our previous investigation³⁰. In brief, SYLGARD silicon elastomer 184 and SYLGARD silicon elastomer 184 curing agents were mixed in a 10 : 1 ratio and air bubble was removed from the mixture by vacuum. The polymer mixture was poured onto a silicon master, which was originally patterned by a photolithography method. After curing at 60°C for 1 h, the flexible elastomeric stamp was removed from the silicon master. The freshly-prepared stamp was cleaned with ethanol and dried under nitrogen atmosphere. The stamp can be used for the generation of more than 100 patterns without loss of its features. Experimental detail of the scanning electron micrograph (SEM) was elaborated in our previous work³⁰.

Anthraquinone-2-sulphonic acid sodium salt monohydrate (0.25 g), 5-sulphosalicylic acid dihydrate (5.34 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.9 g) were dissolved in 25 ml of DI water (called 'solution A'). The substrates patterned with $\text{PyC}_{11}\text{SH}/\text{PM}$ were placed in this solution using clamps. An aqueous solution of pyrrole (150 μl in 25 ml of DI water) was then added slowly with mild stirring. After polymerization, the substrates were taken out, washed with distilled water and then dried under a stream of nitrogen.

A schematic diagram for the generation of $\text{PyC}_{11}\text{SH}/\text{PM}$ pattern by microcontact printing method using an elastomeric PDMS stamp is shown in Schemes 1 and 2.

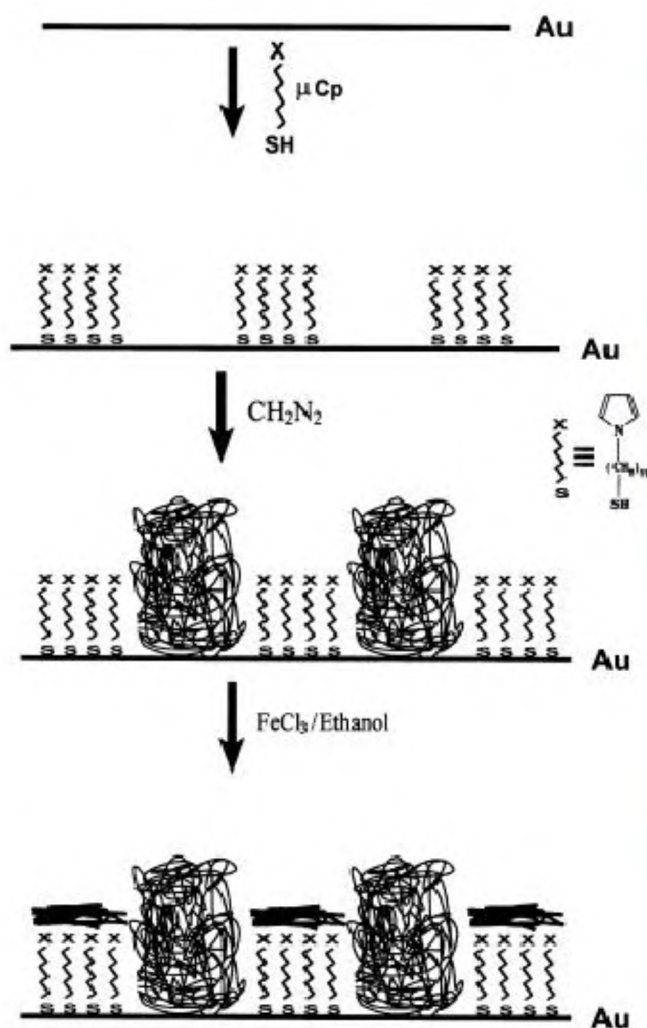


Scheme 1. Schematic diagram of microcontact printing (μ -CP) of polypyrrole/polymethylene pattern on Au.

A dilute solution of PyC₁₁SH (0.1 mM in ethanol) was applied to the stamp using cotton buds. The excess of thiol was removed by flushing N₂ gas. The thiol-exposed stamp was then transferred onto the gold surface by physical contact (2 s) in order to generate the PyC₁₁SH monolayer-pattern. This patterned substrate was then exposed into a freshly prepared diazomethane solution (~1 M). The concentration of diazomethane solution was calibrated volumetrically. The thickness and the morphology of the polymethylene film were characterized with ellipsometry and AFM studies (details are given in our previous paper³⁰).

The PyC₁₁SH/PM-patterned gold substrate was exposed into a freshly prepared solution A at different time intervals. The polymer pattern is clearly shown in Figure 1 *a–d*. Polypyrrole growth is controlled with the exposure time. In this case, we allowed the polypyrrole to grow for 5 min. If it exceeded this time limit, the polymer completely covered the whole surface and the pattern was not clearly observed. In this case, scotch tape was used to peel off the polymer grown on polymethylene-patterned

surface, because polypyrrole grown on polymethylene surface shows poor adhesion. The monomer-initiated polypyrrole strongly bound with the Au surface through a covalent linkage. Thus, this is a simple way of preparation of polypyrrole pattern on Au surface. The pattern thickness and morphology can be studied either by AFM or SEM. For comparison, the electrochemical polymerization was carried out in presence of 0.05 M pyrrole in 0.1 M Bu₄NPF₆ in CH₃CN, as reported earlier³⁰. The pre-selected potential ranges were scanned between 0.0 and 1.2 V vs Ag wire. Figure 1 *a* and *b* shows the optical microscopy images of polypyrrole/polymethylene-patterned surface. The brighter portions correspond to the polymethylene-covered surface and the coloured portions are due to the polypyrrole-modified surface. The polypyrrole/polymethylene-pattern was also generated with the electrochemical polymerization method (Figure 1 *c* and *d*). The brighter areas correspond to the polymethylene-covered surface and the darker areas correspond to the polypyrrole-modified surface. Figure 2 shows an atomic force microscopy (AFM) image with a pattern of polypyrrole printed on



Scheme 2. An outline for the generation of polypyrrole/polymethylene pattern on Au by chemical polymerization.

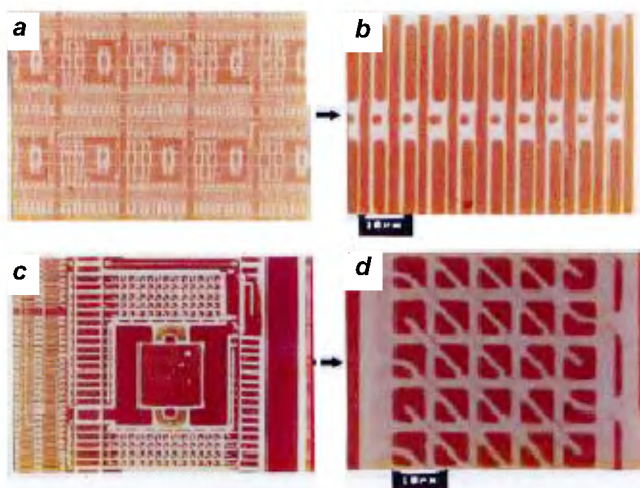


Figure 1. Optical micrographs of polypyrrole/polymethylene-patterned on Au surface prepared by chemical method (*a* and *b*) and by electrochemical method (*c* and *d*).

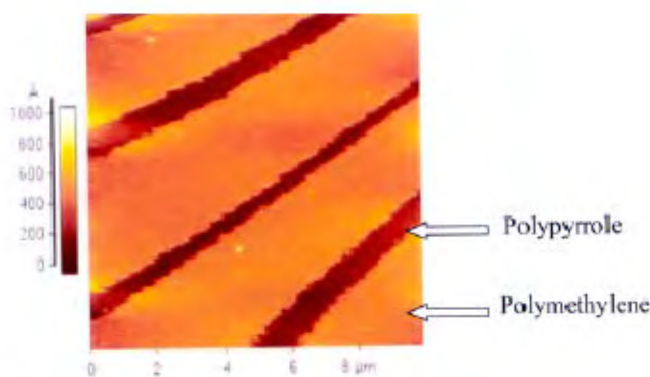


Figure 2. AFM image for polypyrrole/polymethylene pattern on Au.

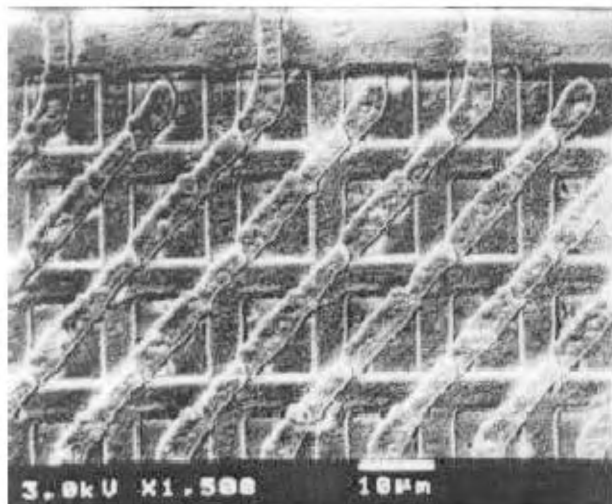


Figure 3. SEM images for patterned silicon master (obtained from commercial sources).

gold surface. The arrow mark shown in the bright yellow colour pattern refers to polymethylene grown on gold surface. The dark brown portion indicates the polypyrrole-patterned surface. The SEM of the patterned silicon wafer is shown in Figure 3, which was generated by conventional photolithography technique. The width of the crossline is found to be around 5 μm . Such conducting polymer-patterned surface can be used in sensor and optoelectronic applications.

In conclusion, the polypyrrole/polymethylene pattern can be generated on gold surface using microcontact printing techniques. The polypyrrole was grown selectively on pyrrole terminal alkanethiol-patterned surface, since pyrrole functions as a nucleating site for the growth of polypyrrole. These polymer patterns show strong adhesion with the gold surface, which was confirmed by scotch-tape peeling test.

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On the origin of non-uniform surface electrochemical potentials on the Delhi iron pillar

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The origin of non-uniform surface electrochemical potentials on the Delhi iron pillar has been addressed based on modern electrochemical theory of passivation. Surface potentials have been related to the differences in thickness and nature of the protective passive film on the exposed surface of the pillar. The most protective passive scale is present in the upper region of the pillar.

THE corrosion-resistant Delhi iron pillar has been attracting the attention of archaeologists, scientists, engineers and scholars for well over two centuries, eager to unravel the

many hidden mysteries of the pillar¹. Several new insights on the Delhi iron pillar have been obtained recently². The excellent atmospheric corrosion resistance of the pillar has been attributed to the formation of a protective passive film on the surface. The nature of this protective passive film has been elucidated³ by analysing the undisturbed rust of the pillar utilizing modern characterization methods⁴. The process of protective film-formation under atmospheric exposure conditions has also been explained³. The protective passive film mechanism of corrosion resistance of the Delhi iron pillar has been recently questioned in the press, wherein it was quoted that surface electrochemical potentials measured on the pillar revealed differences⁵. The direct relevance of surface electrochemical potentials (measured in aqueous solutions) to atmospheric corrosion is not evident because alternate wetting and drying cycles are involved in atmospheric corrosion. Moreover, it is now well established that the nature and rates of electrochemical (anodic and cathodic) reactions that occur during atmospheric corrosion vary significantly during the course of *each* wetting and drying cycle⁶. Nevertheless, the development of non-uniform surface electrochemical potentials on the Delhi iron pillar does not negate the protective passive film mechanism of corrosion resistance of the pillar. The present communication will explore the origin of non-uniform surface electrochemical potentials utilizing modern electrochemical theory of passivation.

Passivity of metals has been a subject of significant research. The nature of the passive films that form on a wide variety of materials has been explored utilizing special electrochemical characterization techniques like impedance spectroscopy⁷. The mechanism of passive film-formation can be understood by modern electrochemical theory, with the aid of polarization diagrams. The polarization diagram is a plot between the potential (i.e. the thermodynamic axis) and current density (i.e. the kinetic axis). The changes in the current density as a function of polarization (i.e. deviation of potentials away from equilibrium) are represented in these polarization diagrams, and several processes related to corrosion (and electrochemistry) can be easily understood utilizing these diagrams. The anodic polarization diagram for a metal exhibiting passivity (i.e. condition of corrosion resistance due to formation of an adherent non-dissolving passive film on anodic polarization under oxidizing conditions) is schematically depicted in Figure 1. It must be remembered that experiments have to be performed by controlling the potential and measuring the current (i.e. either potentiostatically or potentiodynamically) rather than vice versa, in order to understand the passivation phenomenon⁸. In the discussion below, it is emphasized that a freshly prepared (and not oxide or surface-film covered) surface is exposed to the aqueous environment and the anodic polarization is begun immediately on immersion. At the equilibrium reversible potential of the metal (E_{rev}), the ex-

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