Photocatalytic Lithography Based on Photocatalytic Remote Oxidation

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Photocatalytic lithography is a method for surface patterning based on photocatalytic remote oxidation. A TiO_2 -coated photomask is faced with a surface to be patterned, and irradiated with UV light. If a glass plate modified with alkyl chains is used, hydrophilic/hydrophobic patterns can be obtained. The alkyl chains in the irradiated regions are removed by oxidative decomposition, and those in the non-irradiated regions are left. Irradiation time is 30–60 s, and resolution is about 5 μm . This technique is potentially applicable to fabrication of biochips, lab-on-a-chip devices and simple electronic circuits.

Keywords: photocatalytic lithography, patterning, active oxygen species

1. Introduction

Since Honda-Fujishima effect [1] was reported, TiO_2 photocatalyst has been applied to self-cleaning glasses, antibacterial tiles and so on, because it decomposes most organic compounds to volatile compounds including CO_2 on the basis of its strong oxidizing power. Recently we found the photocatalytic remote oxidation effect, in which a chemical species generated on a photocatalyst is transported in air to an organic or inorganic substrate and oxidizes it [2, 3]. We have applied the remote oxidation to “photocatalytic lithography”, which allows facile modification and patterning of the solid surfaces [4–6].

2. Photocatalysis

TiO_2 is one of the metal oxide semiconductors. As electrons in the TiO_2 valence band (VB) are photo-excited by UV light to the conduction band (CB), holes are generated in the valence band (Eq. 1), and reduction and oxidation reactions are driven by the excited electrons (e^-_{CB}) and the holes (h^+_{VB}), respectively (Fig. 1).

Photocatalytic reactions may include reduction of oxygen to superoxide, $\text{O}_2^-/\text{HO}_2^\cdot$ (Eqs. 2 and 3) or hydrogen peroxide, H_2O_2 (Eq. 4) and further reduction of H_2O_2 to hydroxyl radical, $\text{HO}^\cdot$ (Eq. 5). Oxidation of water to $\text{HO}^\cdot$ (Eq. 6) or oxygen (Eq. 7) and oxidation of O_2^- to singlet oxygen, $^1\text{O}_2$ (Eq. 8) may also be involved.

Fig. 1. UV light-induced oxidation and reduction of TiO_2 photocatalysis.

Fig. 2. Experimental setup for photocatalytic lithography.

Those active oxygen species oxidizes various compounds. In particular, $\text{HO}\cdot$ oxidizes most organic compounds.

3. Photocatalytic Remote Oxidation

In the remote oxidation in the gas phase, various substances including aromatic and aliphatic compounds are oxidized [3]. In the case of organic polymers such as polyethylene and polystyrene, oxygen-containing groups like carboxyl ($-\text{COOH}$), carbonyl ($>\text{C}=\text{O}$) and hydroxyl ($-\text{OH}$) groups are introduced to the polymer, and finally decomposed to volatile compounds including CO_2 . Monolayers of silane coupling agents on a glass or a metal oxide surface [3] or alkanethiols on a gold substrate [7] can be removed by the remote oxidation. In particular, in the case of a hydrophobic monolayer, the removal converts the surface from hydrophobic to hydrophilic.

Surfaces of gold [7], silver [5], copper [4, 5], silicon [5] and diamond can also be oxidized. Although poly(vinylidene fluoride) is oxidized [8], Teflon cannot be oxidized [8]. Reactivity of the remote oxidation is close to that of Fenton reaction (Eq. 9) and H_2O_2 -UV reaction (Eq. 10), in which hydroxyl radical is generated [8].

4. Photocatalysts

Besides TiO_2 , some other photocatalytic materials including SrTiO_3 and ZnO are active in

the remote oxidation [8]. Deposition of platinum, gold, palladium and silver nanoparticles on the photocatalyst further improves the remote oxidation activity in general. In particular, deposition of platinum increases the rate of remote oxidation by an order of magnitude [8].

5. Typical Procedures

Typical procedures for photocatalytic lithography are as follows. A chromium photomask pattern is formed on an alkali-free glass plate. The mask is coated with a TiO_2 thin film. The film is irradiated with UV light in ethanol-water mixed solution containing H_2PtCl_6 , so that platinum particles are photocatalytically deposited on the film. A substrate to be patterned (e.g., a glass plate modified with octadecyltriethoxysilane, ODS-coated glass plate) is faced with the photocatalyst with an intervening gap (typically ca. $10\ \mu\text{m}$). The TiO_2 film is irradiated with UV light through the photomask, so that the irradiated region of the substrate surface is oxidized (Fig. 2). In the case of the ODS-coated glass plate, the irradiated regions are converted from hydrophobic to hydrophilic, so that hydrophilic/hydrophobic patterns can be prepared. Irradiation time is 30–60 s, and resolution is about $5\ \mu\text{m}$ [5].

6. Mechanisms

Resolution of 5–10 μm was obtained even when the intervening gap between the TiO_2 film and the substrate was $100\ \mu\text{m}$. This is explained in terms of a double excitation scheme, in which not only TiO_2 but also a chemical species diffusing from the TiO_2 surface or the substrate to be oxidized is excited by the incident light [5].

Thus, we proposed a mechanism involving photocatalytic production of H_2O_2 (Eqs. 1 and 4), its desorption, diffusion and photocleavage to $\text{HO}\cdot$ (Eq. 10) and its reaction with a substrate (Fig. 3).

Fig. 3. Mechanisms of photocatalytic remote oxidation.

Fig. 4. Hydrophilic/hydrophobic pattern prepared by photocatalytic lithography.

Actually, we found that H_2O_2 is released to the gas phase from the photocatalysts [9]. Also, we found that the remote oxidation activity was comparable to that of the H_2O_2 -UV reaction at the same H_2O_2 level [10]. These facts support that our scheme is plausible.

7. Advantages and Drawbacks

The photocatalytic lithography as a patterning technology has the following advantages and drawbacks.

- The non-contact treatment does not readily damage the substrate surface.
- Coating and removal of a photoresist is not necessary.
- Control of the atmosphere is not necessarily required.
- The employed near-UV light is safer than UV light with shorter wavelength.
- Dry processes.
- The reaction is mild, so that the process takes time.
- Reactions are limited to some oxidation reactions.

8. Applications

As described above, hydrophilic/hydrophobic patterns can be prepared easily [4, 5]. If the substrate surface was roughened, the initial hydrophobicity and final hydrophilicity are enhanced. In the case of a glass substrate, silica particles can be used to increase the roughness [6]. Gold surface can be roughened by electrodeposition [7]. As a result, contrast of the hydrophilic/hydrophobic patterns is enhanced (Fig. 4).

The present technique might be applicable to lab-on-a-chip, μ -TAS and microreactor devices. Functional molecules including enzymes and cells can be immobilized on the hydrophilic regions, so that chemical sensor arrays and biochips can be prepared on the basis of photocatalytic lithography [7]. If a conducting material (a metal or carbon particle or a conducting polymer) is applied to the hydrophilic regions, a simple electronic circuit would be prepared.

Hydroxyl, carbonyl or carboxyl groups introduced to the substrate surface by the photocatalytic lithography may be used for chemical immobilization of functional molecules (Fig. 5) [7].

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Fig. 5. Functionality patterning by photocatalytic lithography.

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