

Mechanisms and Resolution of Photocatalytic Lithography

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Remote oxidation via the gas phase by the TiO₂ photocatalyst was exploited for a novel technique for solid surface patterning, photocatalytic lithography. A TiO₂-coated photomask was placed on an organic or inorganic substrate to be patterned with a small gap (12.5–100 μm), and irradiated with UV light. Heptadecafluorodecyltrimethoxysilane-, octadecyltriethoxysilane-, and methyltriethoxysilane-coated glass plates, a silicon plate, and a copper plate could be patterned in ≥ 10 min with resolution of 10 μm or better. Such resolution could be obtained even when the intervening gap between the TiO₂ film and the substrate was 100 μm. This may be explained in terms of a double excitation scheme, in which not only TiO₂ but also a chemical species diffusing from the TiO₂ surface or the substrate to be oxidized is excited by the incident light.

Introduction

TiO₂ photocatalysts¹ have been studied extensively and applied to self-cleaning, self-sterilizing, and deodorizing coatings.² Recently we have reported remote oxidation of organic and inorganic materials by the TiO₂ photocatalyst.^{3–6} This is a phenomenon that a chemical species generated at the TiO₂ surface by UV irradiation diffuses through the gas phase and oxidizes organic and inorganic substances. Some other groups^{7–9} have supported our results experimentally. It has been pointed out^{7,8,10} that the remote oxidation via the gas phase might be involved in the conventional remote oxidation by TiO₂ via solids.^{10–13} One can oxidize and hydrophilize organic compounds including polystyrene and polyethylene,⁴ inorganic materials including silicon,⁶ diamond,^{5,9} and silicon carbide,⁹ and noble metals including copper and silver⁶ by the remote oxidation.

In our preliminary work,⁶ we have developed a novel technique for the patterning of solid surfaces on the basis of the remote oxidation via the gas phase, as photocatalytic lithography. A TiO₂ film placed onto a solid surface to be patterned was irradiated with UV light through a patterned photomask, and the corresponding pattern was observed on the solid surface. The present method requires neither a photoresist nor special equipments other than a light source. In addition, this simple noncontacting process would not cause any surface damages.

With this method, hydroxyl, carbonyl, or carboxyl groups can be introduced to specific regions of solid surfaces easily, so that the regions would be selectively modified with functional molecules such as dyes, catalysts, proteins, and DNAs via those groups to obtain display devices, chemical chips, and biochips.

However, in our preliminary results, the resolution was as low as 100 μm. Diffraction of the incident light at the photomask

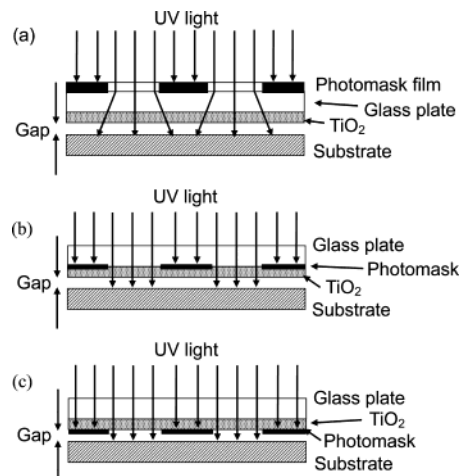


Figure 1. Experimental setups for the photocatalytic lithography: (a) conventional photomask/glass plate/TiO₂ assembly; (b) glass plate/photomask/TiO₂ assembly; (c) glass plate/TiO₂/photomask assembly.

might not be negligible because the distance between the TiO₂ coating and the mask was very long, about 1 mm (Figure 1a). Here we coated a photomask directly with a TiO₂ film to minimize the distance (Figure 1b). As a result, resolution was greatly improved to around 5 μm.

Additionally, comparison of the remote oxidation, which does not involve holes and electrons as direct reactants with substrates, with conventional TiO₂ photocatalysis, which may involve holes and/or electrons, would give important information about mechanisms of the latter, which has not yet been fully understood.

Experimental Section

Preparation of TiO₂ Coatings Combined with Photomasks. TiO₂ coated on a photomask (glass plate/photomask/TiO₂ assembly; Figure 1b) and TiO₂ supporting a photomask (glass plate/TiO₂/photomask assembly; Figure 1c) were prepared. The former was prepared as follows: A photomask was

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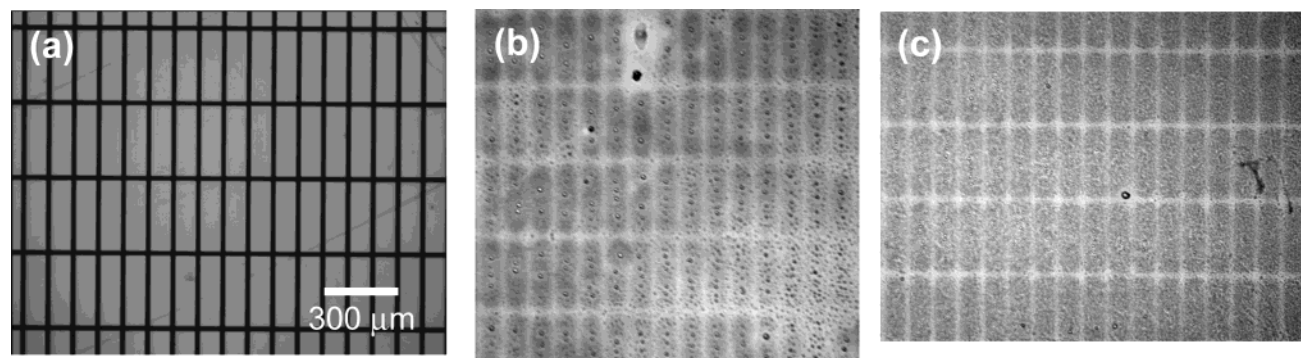


Figure 2. (a) Bright-field micrograph of the photomask used and differential interference contrast micrographs of (b) HDFs- and (c) ODS-coated glass plate surfaces patterned by the photocatalytic lithography (spacer thickness, 12.5 μm ; light intensity, 100 mW cm^{-2} ; irradiation time, 10 and 20 min for parts b and c, respectively).

prepared by partially coating a nonalkaline glass plate (thickness, 0.8 mm) with a Cr thin film (thickness, ca. 150 nm). The photomask surface was cleaned by exposing it to UV light with a black-light-type lamp. The surface was coated with TiO_2 from an alkoxysilane (as a binder) solution containing anatase TiO_2 particles (average diameter, 60 nm) by spin-coating at 350 rpm for 5 s. The film was annealed at 150 $^\circ\text{C}$ for 10 min.

The latter was prepared as follows: A nonalkaline glass plate was coated with TiO_2 in a similar manner, then partially coated with a poly(methyl methacrylate)-based polymer including black inorganic pigments. The resulting TiO_2 coatings were irradiated with a black-light-type lamp ($\sim 300\text{--}400\text{ nm}$, $\sim 1\text{ mW cm}^{-2}$) overnight before each experiment to clean the surface.

Several different patterns, including rectangular lattice patterns and bar-graph-like patterns (frequently used to check patterning resolutions), were used.

Substrates to be Patterned. A glass plate treated with hepta-decafluorodecyltrimethoxysilane ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$; HDFs), octadecyltriethoxysilane ($\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{OC}_2\text{H}_5)_3$; ODS), or methyltriethoxysilane ($\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$; MTS), a silicon single-crystal plate (n-type conductive silicon), or a copper plate was used as a substrate.

An HDFs-, ODS-, or MTS-coated glass plate was prepared as follows: A glass plate was treated with 1 M aqueous NaOH for 1 h and rinsed thoroughly with water. The glass plate was dried and soaked in a 10 vol % methanol solution of HDFs, 10 vol % toluene solution of ODS, or 10 vol % ethanol solution of MTS for 30 min.

Patterning and Evaluation. The substrate was placed on the TiO_2 coated on the photomask with a small intervening gap. The gap was controlled by use of polyimide films (Nilaco; thickness, 12.5–100 μm). The TiO_2 coating was irradiated with Hg–Xe lamp (Luminar Ace, Hayashi Tokei; 100 mW cm^{-2}) from the back, unless otherwise noted, under the ambient conditions. As we have reported previously,³ the remote oxidation rate depends strongly on the oxygen concentration, but poorly on the humidity. Therefore, reproducible data can be obtained in ambient air.^{4,6}

The patterned sample was refrigerated at 0 $^\circ\text{C}$, and then the sample was observed by means of differential interference contrast microscopy using a microscope BX51 (Olympus) under ambient conditions, so that the hydrophilic/hydrophobic patterns were visualized by frosts deposited. In the case of a patterned Cu plate, the irradiated region was matted and darkened, so that the patterns could be observed by means of bright-field microscopy. An atomic force microscope (AFM; SN-3800, Seiko Instruments Inc.) was also used.

Results and Discussion

Photocatalytic Lithography. In our preliminary report,⁶ photomask/glass plate/ TiO_2 assembly was employed, and the distance between the TiO_2 film and the photomask was about 1 mm (=the thickness of the glass plate). Therefore, the resolution of the patterning was as low as 100 μm , probably due to diffraction of incident light at the edge of the photomask (Figure 1a). In the present work, to minimize the effect of diffraction, a photomask was directly coated with a TiO_2 film (glass plate/photomask/ TiO_2 assembly, Figure 1b).

As a result, in the patterning of an HDFs-coated glass plate, the resolution was 20 μm or better (Figure 2b). The irradiation time was 10 min, and the gap between the TiO_2 and the substrate was 12.5 μm . The pattern was not observed when a photomask without TiO_2 was used, even after 60-min irradiation. The pattern was also visualized by evaporation of a 0.3 μM methanol solution of rhodamine 6G. On the basis of the thus obtained fluorescence microgram, rhodamine 6G was found to be localized in the irradiated regions. This indicates that the irradiated regions exhibit higher affinity to methanol than do the nonirradiated regions.

We also examined changes in the hydrophilicity of the HDFs-coated glass surface, by using a TiO_2 -coated plate without a photomask instead of the TiO_2 -coated photomask. As a result, the water contact angle of the HDFs-coated glass plate surface decreased from 90–100 to ca. 10 $^\circ$ over 10 min irradiation, indicating an increase in the surface hydrophilicity. This should be because the HDFs layer was decomposed by the remote oxidation to expose the OH groups on the bare glass surface. Actually, similar increases in hydrophilicity have been observed for ODS-coated glass surfaces,^{4,6} and the removal of the ODS layer has been verified by means of XPS.⁴ These support that the patterns obtained here are based on a difference in the hydrophilicities between the irradiated and nonirradiated regions, as we have reported previously.⁶

Although the irradiation time of 10 min is longer than the conventional photolithography, the present photocatalytic lithography does not require coating and removing processes of photoresists, which take time.

Patterning of Various Substrates. Better resolution was observed for the ODS- (Figure 2c) and MTS-coated glass plates and silicon and Cu plates. ODS and MTS layers are decomposed and removed by the remote oxidation. Silicon and Cu are oxidized to be corresponding oxides.⁶ Irradiation time necessary to observe the patterns were 20 min, 10 min, 20 min, and > 10 h for ODS-coated glass, MTS-coated glass, silicon, and Cu plates. In the patterning of the Cu surfaces, a pattern of bands with a width of 5 μm could be formed (Figure 3). The dots

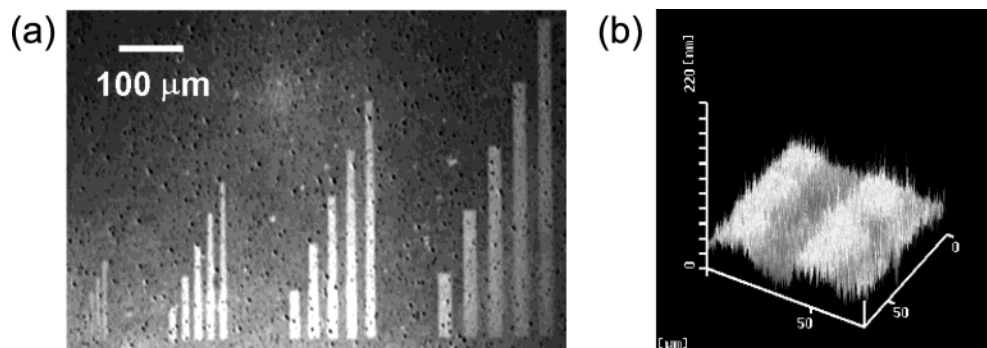


Figure 3. Micrograph of the Cu plate surfaces patterned by the photocatalytic lithography (spacer thickness, 12.5 μm ; light intensity, 100 mW cm^{-2} ; irradiation time, 24 h).

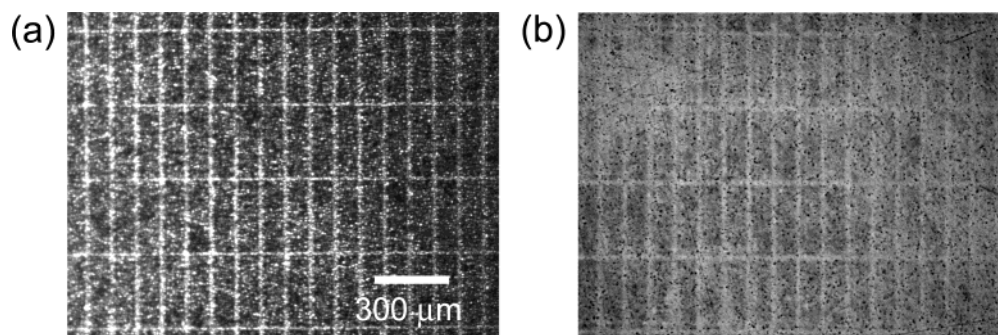


Figure 4. Micrographs of the patterned Cu surfaces after the photocatalytic lithography (spacer thickness, (a) 12.5 μm or (b) 100 μm ; light intensity, 100 mW cm^{-2} ; irradiation time, 24 h; the photomask shown in Figure 2a was used).

seen in the microgram (Figure 3a) have also been observed before the patterning. Those may be corrosion pits generated immediately after the polishing.

Dependence on the Gap between TiO_2 and Substrates. We also varied the distance between the TiO_2 coating and substrates (HDFS-, ODS-, and MTS-coated glass plates and a Cu plate) from 12.5 to 100 μm , and found that the resolution of 20 μm could be obtained regardless of the distance (Figure 4). If the chemical species diffusing from the TiO_2 surface reacts directly with the substrate, such as HDFS in the ground state, it should be impossible to obtain the resolution of 20 μm when the TiO_2 -substrate distance is 100 μm as far as the species diffuse not only longitudinally but also laterally. There are two possibilities instead: the target substrate such as HDFS is excited by UV light and reacts with the chemical species diffusing from the TiO_2 , or the chemical species diffusing from TiO_2 is excited by UV light to be an active, short-lived secondary species, and then the secondary species react with the substrate. In the latter case, the lifetime of the excited secondary species is such short that only those excited near the target substrate surface react with the substrate. Namely, not only TiO_2 but also the substrate surface or diffusing species in the vicinity of the substrate surface should be photoexcited.

Use of the Masked TiO_2 . If such a double excitation scheme is not considered, we have to assume that the active species detached from the TiO_2 surface are transported perpendicularly to the target substrate, although this may not be very plausible.

Then, the patterning behavior was further examined by using a TiO_2 -coated glass plate that supports a photomask as shown in Figure 1c (glass plate/ TiO_2 /photomask assembly). First, the TiO_2 was irradiated from its back as shown in Figure 5, parts a and b, so as to irradiate the HDFS layer partially. In these cases, patterns corresponding to the photomask were obtained by 5- or 15-min irradiation when the gap between the mask and the HDFS layer was 12.5 or 100 μm , respectively. This is

quite reasonable, if either the double excitation scheme or the perpendicular transport scheme is valid. Incidentally, when a photomask without TiO_2 was used, the HDFS-coated glass plate remained hydrophobic and no pattern was obtained.

Next, TiO_2 was irradiated from its front through the HDFS-coated glass plate (Figures 5c and d), so as to irradiate the HDFS layer entirely, while the TiO_2 surface partially. In this case, a pattern was observed for 5-min irradiation when the gap was 12.5 μm (Figure 5c), although the pattern was less clear than those shown in Figure 5, parts a and b. In the case where the gap was 100 μm , however, no significant pattern was observed at any time examined (5, 10, 15, 30, and 60 min), and the surface was almost uniformly oxidized in 15 min (Figure 5d). Since the pattern was not obtained even when the irradiation time was shortened, the reason was not overexposure.

If the perpendicular transport of an active species holds, the surface should be patterned in both of the cases. On the other hand, the above results can be explained in terms of the double excitation scheme, in which the oxidation requires both the diffusing species and the incident light. In a relatively short time scale (i.e., ≤ 5 min), the diffusing species may be still localized near the bare (and irradiated) TiO_2 regions. In the case where the gap is 12.5 μm , areas of the target surface in contact with the localized regions are oxidized, and the relatively unclear pattern is obtained in 5 min. However, the diffusing species diffuses not only vertically but also laterally. In the case where the gap is 100 μm , which is longer than the width of the masked TiO_2 region (20 μm), the localized regions (of the diffusing species), which have been separated by the masked region, are overlapped each other before the regions reach the target surface. Therefore, the surface is oxidized uniformly and no patterns are obtained.

Possible Chemistry. In the present stage, it is not known whether diffusing species or the substrate to be oxidized is excited. If the former is excited, taking into account that the

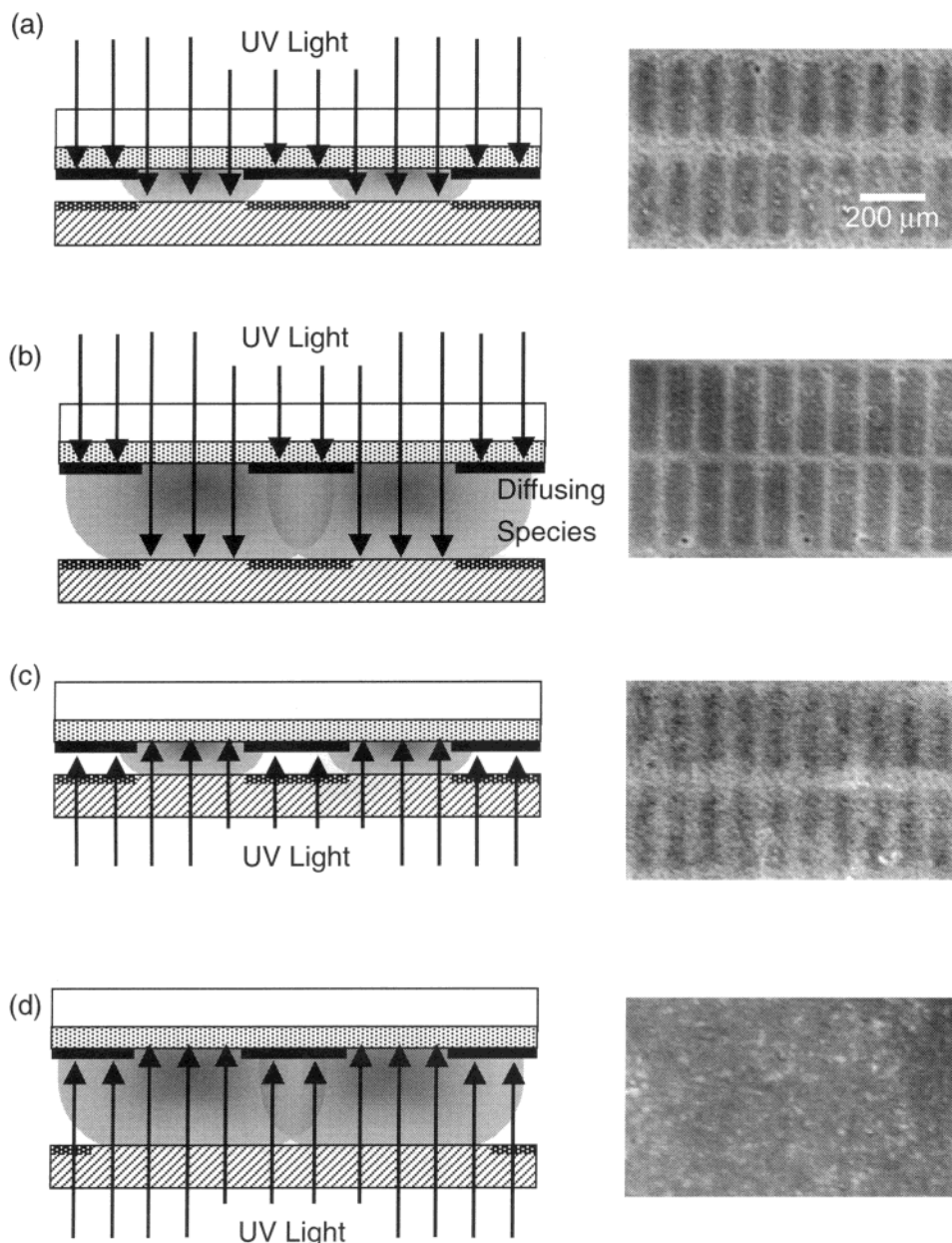


Figure 5. Experimental setups and corresponding results of photocatalytic lithography using the masked TiO₂ (glass plate/TiO₂/photomask assembly) (patterned substrate, HDFS-coated glass plates; light intensity, 100 mW cm⁻²; irradiation time, (a, c) 5 or (b, d) 15 min).

active species attacking substrates directly may be $\cdot\text{OH}$,⁴ the diffusing species may be H₂O₂ or HO₂. H₂O₂ could be photodecomposed to $\cdot\text{OH}$ by UV light of wavelengths shorter than 365 nm.¹⁴



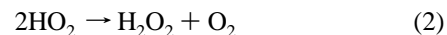
Transmittance of the TiO₂-coated glass plate was ca. 5, 20, or 50% at 280, 300, or 320 nm, respectively. Therefore, H₂O₂ could be photodecomposed, even if it is slow. Incidentally, absorbance of 0.04 M aqueous H₂O₂ was 0.18, 0.05, or 0.01 at 280, 300, or 320 nm, respectively (light path length, 1 cm), indicating that H₂O₂ absorbs light at these wavelengths.

H₂O₂ reportedly forms hydroperoxo, superoxo, and peroxy species on TiO₂ surfaces.¹⁵ However, after the surface is saturated, H₂O₂ generated continuously should be released from the surface.¹⁶ To verify whether thus released H₂O₂ diffuses into air, we prepared a flow-through porous TiO₂ cell (90 × 90 × 4 mm), and air (relative humidity, 50%) flowed through the

cell that was irradiated with UV light (2×10^{23} photons) was flushed through water. As a result, we have detected H₂O₂ in the solution by peroxidase-based colorimetric technique (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) was used as a redox indicator). As a result, 2.9×10^{-8} mol of H₂O₂ was detected. No color change was observed when peroxidase was not used.

Apparent quantum yield (=2 × the number of H₂O₂ molecules detected/the number of photons) was estimated to be 1.8×10^{-7} . On the other hand, the quantum yield of the remote oxidation is $>10^{-5}$ when the gap between the TiO₂ and the target polymer (polyethylene and polystyrene) was 50 μm.⁴ Since the remote oxidation rate decreases as the gap increases, the 2 orders of magnitude lower quantum yield is not unreasonably low, considering the distance between the TiO₂ and the H₂O₂-collection vial, which was several tens of centimeters.

On the other hand, HO₂ could undergo disproportionation,



and the generated H_2O_2 could be photodecomposed to give $\bullet\text{OH}$ (eq 1). However, this bimolecular process may be very unlikely unless HO_2 is adsorbed on the target surface and diffuse at the surface freely.

In any cases, the double excitation mechanism, which involves excitation of diffusing species in the vicinity of the substrate surface or the substrate itself as well as excitation of TiO_2 , is advantageous to obtain high resolution in application of the remote oxidation to solid surface patterning. If highly straight light beam and a highly uniform TiO_2 film that does not scatter light beams are available, the resolution would approach the scale of the light wavelength, namely the submicrometer level.

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