CHEMISTRY LETTERS, pp. 379-382, 1993.

Photocatalytic Micropatterning of Titanium Oxide Surface with Platinum

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Platinum (Pt) micropatterns were fabricated photocatalytically on titanium oxide (TiO_2) surface by projecting a reduced light image of a photomask. Negative and positive Pt patterns on TiO_2 with the spatial resolution better than 10 μm were obtained by photoreduction of $PtCl_4^{2-}$ to Pt in aqueous K_2PtCl_4 solution and photoetching of the deposited Pt in aqueous HCl solution, respectively.

Platinized titanium dioxide electrodes or particles (Pt/TiO_2) are of particular importance owing to the excellent photocatalytic activities towards various redox reactions including photodecomposition of water.1-5) Commonly, Pt/TiO_2 particles are prepared by reduction of Pt ions and subsequent deposition of Pt on TiO_2 in suspended TiO_2-Pt ion solution. In such cases, small Pt islands are randomly deposited to the TiO_2 surface and, therefore, a role of spatial arrangement of Pt for the photocatalytic activity of TiO_2 cannot been studied. Previously, Hiramoto et al. demonstrated that metal micropatterns (≈ 10 μm) on semiconductor electrodes led to improvement of their photoredox abilities.6) Although spatial arrangement of reaction sites on materials surface is certainly promising to achieve efficient redox systems, micropatterning of material surface with well-defined metal structures requires in general complicated procedures represented by photolithographic methods.6) On the other hand, photoelectrochemical patterning of semiconductor surface with metals has been reported based on photoirradiation of the surface through a photomask.7) However, the spatial resolution obtained by such a method is not satisfactorily.7) A new method for producing metal micropatterns on the semiconductor surface with arbitrary spatial patterns is clearly necessary to study spatial arrangement effects on the photocatalytic activities of metalized semiconductor materials.

It is well known that TiO_2 surface can be deposited with noble metals (M) such as Pt, Pd, and so forth through reduction of the relevant ion (M^{n+}) at the TiO_2 - M^{n+} solution interface by photogenerated electrons in the conduction band of TiO_2.8-10) Contrarily, if the

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energy level of the valence band edge of TiO_2 is more positive than that of a M/M^{n+} redox couple, M deposited on TiO_2 will be reoxidized and etched by photogenerated holes in the valence band. Therefore, proper choices of a M/M^{n+} couple and an optical configuration for irradiation will lead to microdeposition and microetching of M on TiO_2 in arbitrary spatial patterns. In the present letter, we demonstrate photocatalytic micropatterning of TiO_2 with Pt. Particular emphasis of the study is fabrication of a positive or negative Pt micropattern on the TiO_2 surface by the identical optical alignment without complicated photolithographic procedures.

An optical system for micropatterning of Pt on TiO_2 is illustrated in Fig. 1. A 100 W super high-pressure Hg lamp (Ushio, USD-10) was used as a light source. A photomask was illuminated through a condenser lens and a glass filter ($300 < \lambda < 430$ nm), and the photomask image was projected to the TiO_2 surface which contacted with a deposition or etching solution. In the present experiments, we used an objective lens with magnification of 10, so that the spatial pattern is reduced to the one tenth of the original mask pattern at the TiO_2 surface. An aqueous solution of K_2PtCl_4 (10 mM) or HCl (1 M) was used for photodeposition or photoetching of Pt on TiO_2, respectively. The thickness of the solution in Fig. 1 was adjusted to 0.5 mm. Polycrystalline titanium films with a thickness of 0.2 µm were evaporated on ITO glass plates by sputtering, and the films were anodically polarized in an aqueous H_2SO_4 (0.5 M) solution at the potential of +10 V-DC (vs. a Pt wire counter electrode) for 30 s to grow the TiO_2 layer on Ti. The samples were rinsed with pure water and treated in acetone vapor prior to experiments. The thickness of the oxide layer was estimated to be 17 nm by ellipsometry.

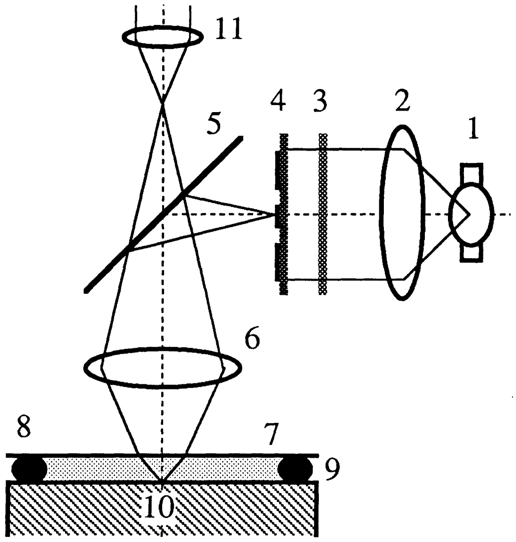

Fig. 1. Optical system for micropatterning; 1. super high pressure Hg lamp (USD-10, Ushio), 2. condenser lens, 3. glass filter (BG-1, Melles Griot), 4. photomask, 5. half mirror, 6. objective (UV Fluor 10, Nikon), 7. cover glass, 8. solution, 9. Viton packing, 10. titanium oxide substrate, 11. eyepiece

When TiO_2 immersed in K_2PtCl_4 solution is illuminated with UV light, Pt ions are reduced at the TiO_2 - solution interface and Pt is deposited to the illuminated area on TiO_2. Photoillumination was thus conducted by the present experimental setup. A Pt micropattern was fabricated on the TiO_2 surface as shown in Fig. 2, where deposited Pt lines with 10 µm width (dark region) and the TiO_2 surface (bright region) were clearly resolved. Since it has been reported that photogenerated electrons are trapped at surface sites for polycrystalline TiO_2 films as in the present case,[9] Pt ions react with the electrons at the TiO_2 surface under photoillumination. It is noteworthy that K_2PtCl_4 itself absorbs UV light and Pt ions are expected to be reduced to Pt. To test such the possibility, analogous experiments were performed in the HOPG (Le Carbone-Lorraine) - K_2PtCl_4 system. However, we could not observe deposition of Pt on HOPG. Clearly, photodeposition of Pt on TiO_2 is responsible for the electrons in the conduction band of TiO_2. Positive holes in the valence band will be captured by water.

When the platinized TiO_2 surface immersed in aqueous 1M HCl solution is illuminated with UV light, Pt is oxidized by photogenerated holes in TiO_2 and dissolved into the solution. Thus, the Pt film on TiO_2, prepared by the method explained above without the photomask, can be etched in HCl solution to give a Pt micropattern. As clearly seen in Fig. 3, a Pt micropattern was fabricated by photoetching, whose pattern was reversed to that in Fig. 2. During photoillumination, Pt ions dissolved into the HCl solution may be reduced again by the electrons in TiO_2. However, since the photoetching rate of Pt is much faster than the Pt deposition rate in aqueous 1 M HCl solution, the Pt layer on TiO_2 is etched in total upon photoillumination.

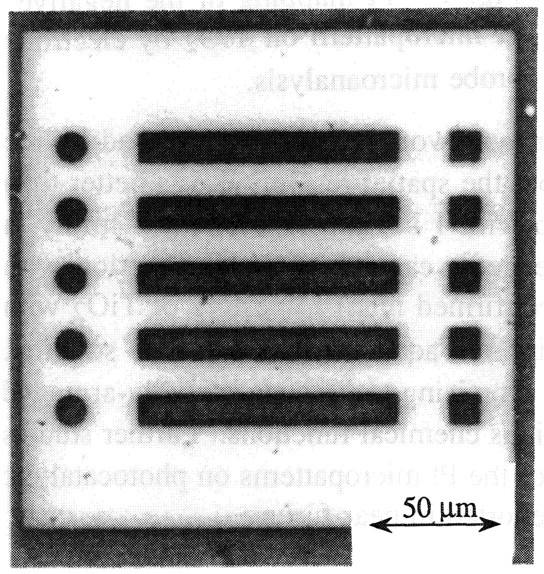

Fig. 2. Negative Pt micropattern on TiO_2 prepared by photodeposition of Pt on TiO_2 in K_2PtCl_4 solution for 30 min.

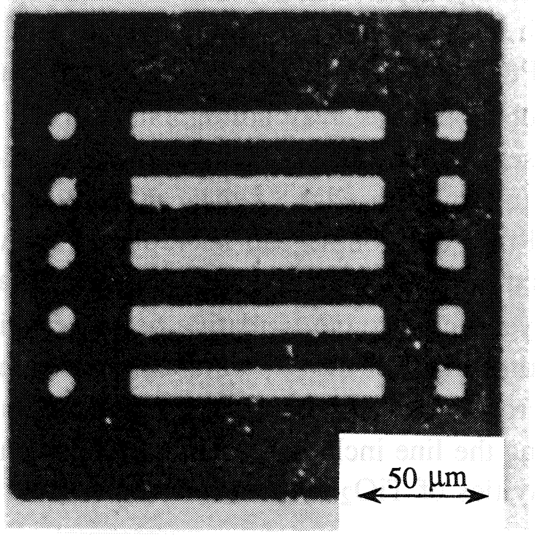

Fig. 3. Positive Pt micropattern on TiO_2 prepared by photodeposition of Pt on TiO_2 for 30 min, followed by photoetching of Pt on TiO_2 in HCl solution for 18 min.

The Pt micropatterns on TiO_2 were analyzed by several methods. The thickness of the deposited Pt layer was estimated to be ≈ 40 nm (deposition time ≈ 30 min) by scanning tunneling microscopy. Energy dispersion X-ray spectroscopy of the pattern showed a characteristic Pt Mα line around 2.1 keV, confirming deposition of Pt on TiO_2. Elemental analysis by electron probe microanalysis on the deposited pattern also proved the spatial pattern of Pt on TiO_2, where the bright dots and dark region represented Pt and the TiO_2 surface, respectively (Fig. 4). Although the line patterns of Pt in Fig. 4 (5 µm line) is not clearly resolved due to the very thin Pt layer on TiO_2 and a low signal to noise ratio of the meaurements, the Pt pattern in Fig. 4 agreed with that in Fig. 2 (10 µm line).

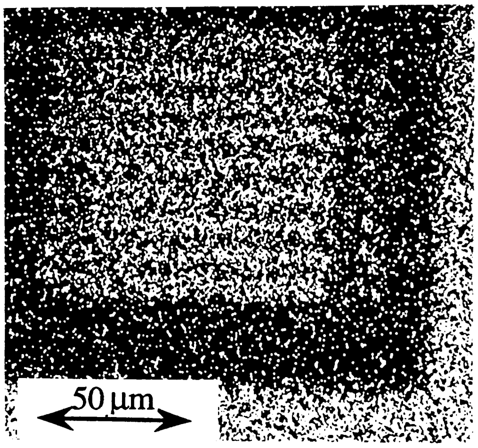

Fig. 4. Pt mapping of the negative Pt micropattern on TiO_2 by electron probe microanalysis.

Characteristic features of the present photocatalytic micropatterning of Pt on TiO_2 are as follows. Firstly, it is worth noting that both positive and negative Pt micropatterns can be fabricated by the use of an identical photomask through a proper choice of deposition/etching solution. Microfabrication of metal patterns by photolithography usually involves several complicated processes. However, the present method is very simple and easy to be performed. Secondly, projection of a reduced photomask image under an optical microscope is advantageous to fabricate micropatterns. Besides the present method, we performed the analogous experiments with the photomask being contacted with TiO_2 in K_2PtCl_4 solution. However, the spatial pattern of Pt obtained was very ambiguous and the resolution was worse than that produced by the present method in Fig. 1. For the projection method, the spatial resolution was better than 10 µm and the edge of the pattern was very sharp with 1 - 2 µm resolution. Thirdly, a Pt/Pt^{2+} ion couple can be replaced by various reagents capable of redox reaction with electrons and holes in TiO_2. Experimentally, we confirmed micropatterning of TiO_2 with polyaniline through oxidative polymerization of aniline in aqueous aniline sulfate soluiton. Optimization of the experimental conditions will be promising to produce spatially-arranged micropatterns on semiconducting materials with various chemical functions. Further studies along the line including spatial arrangement effects of the Pt micropatterns on photocatalytic activities of TiO_2 are now in progress and will be reported in near furture.

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(Received December 2, 1992)