Photoelectrochemical Fabrication of Submicrometer Platinum Pattern
on Titanium Dioxide Single Crystal Surface

Hidekazu Ishii, Saulius Juodkazis,*[†,††] Shigeki Matsuo, and Hiroaki Misawa*
Department of Ecosystem Engineering, Graduate School of Engineering, The University of Tokushima
2-1 Minamijyosanjima, Tokushima 770-8506
[†]*The Satellite Venture Business Laboratory, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506*

Submicrometer patterning of TiO_2-rutile single crystal surface by Pt was accomplished by means of photocatalytic reduction of $PtCl_4^{2-}$ to Pt in an aqueous solution of H_2PtCl_6. The patterns of Pt were fabricated along focal point traces of 380 nm wavelength excitation laser beam on the surface of rutile substrates.

Platinized titanium dioxide electrodes and particles are of particular importance due to their photocatalytic behavior in redox reactions as photodecomposition of water,[1,2] photocatalytic oxidation employed for biotechnological water[3] and soil[4] regeneration. Previously, it was shown that photocatalytic properties of metalized semiconductors are enhanced when pattern dimensions are reduced to micrometer size.[5] Also, it was demonstrated photoelectrochemical patterning of metal on the semiconductor surface through a photomask,[6,7] however, the spatial resolution obtained by such a method is still in micrometer region.[7] Photocatalytic behavior which is based on charge transfer in TiO_2-Pt-electrolyte system is to be better understood and controlled when Pt pattern size is reduced to nanometer scale.

In this letter, we report enhancement in spatial resolution of TiO_2 surface patterning by Pt up to submicrometer dimension. The mechanism of growth of nanometer-sized Pt islands in the focal point of laser beam is also discussed.

An optical system for micropatterning comprises of a femtosecond laser, second harmonic generator (Spectra Physics, Tsunami), and an optical microscope (Olympus, IX70). An objective lens (magnification, ×100) with high numerical aperture, NA=1.35, was employed in order to localize excitation on the surface of substrate. A piezo-actuator equipped to the stage of the microscope was driven according to programmed deposition patterns. The typical stage velocity was 0.5 μm/s. The excitation wavelength was changed within (380~428) nm range to meet resonant conditions of TiO_2-rutile substrate excitation (indirect optical band gap of 3.1 eV[8]) and, also, to check the possibility of Pt ions reduction directly from a sample solution by UV light absorption. The pulse duration and the repetition rate of the laser beam were 80 fs and 82 MHz, respectively.

TiO_2-rutile plates of (110) face surface were utilized as substrates. The roughness of the surface was about 4 nm (peak value) as measured by an atomic force microscope (AFM, Seiko Instruments, SPI 3700). The aqueous solution of H_2PtCl_6 (20 mmol/dm³) was placed between a substrate and an etched (10×10 mm² with 100 μm depth) cover glass and was set on the stage of the microscope. Optical density of the solution was lower than $5×10^{-2}$ for 10 mm optical path length at any employed excitation wavelength. At such experimental conditions absorption of excitation light by the solution was negligible in comparison to resonant absorption in TiO_2.
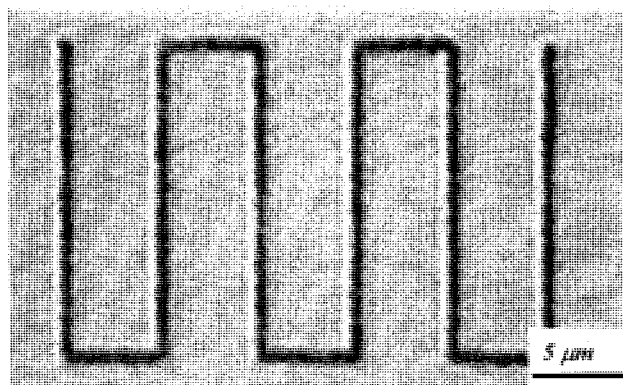

Figure 1. Top image of Pt pattern (dark region) produced on the surface of TiO_2 (110). Irradiation wavelength = 380 nm, laser power = 158 μW, stage velocity = 0.432 μm/s.

An optical image of Pt trace of ~700 nm in width on the rutile surface is presented in Figure 1, when 158 μW irradiation power at the 380 nm wavelength was employed; the stage velocity was 0.43 μm/s. According to the optical image whose spatial resolution is ~300 nm, detectable roughness of the Pt line could not be observed. However, an AFM image of a Pt pattern obtained at similar experimental conditions shows that the Pt line is formed by assembly of 50~200 nm-sized Pt islands as depicted in Figure 2. No Pt deposition was observed whenever the wavelength longer than that of fundamental absorption of TiO_2 at 400 nm was employed, e.g. no Pt pattern was produced by a 428 nm excitation beam. This supports photocatalytic
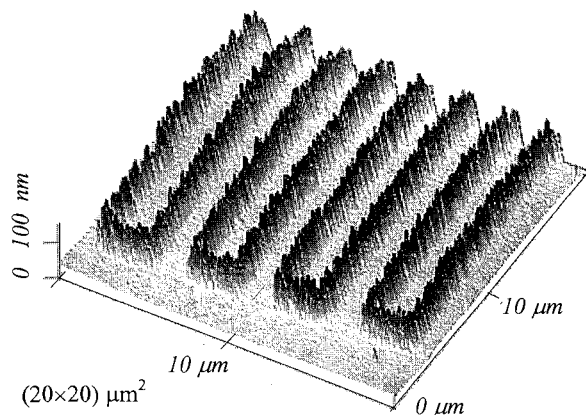

Figure 2. Atomic force microscope image of Pt pattern fabricated on TiO_2-rutile surface. Irradiation wavelength = 380 nm, laser power = 125 μW, stage velocity = 0.4 μm/s.

mechanism of Pt formation[2,7] when photogenerated electrons in the pre-surface area of TiO_2 substrates are responsible for initiation of the reduction of $PtCl_4^{2-}$ to Pt. The electrons are trapped at surface sites where Pt reduction can be initiated. The points where Pt was once reduced establishes metal-solution contact which, in turn, creates potential dip for the arriving electrons from TiO_2 volume.[2] Such Pt growth mechanism is consistent with our experimental data as well: simultaneous growth over the area more extended than illuminated one; dots like structure of the Pt pattern (Figure 2) implies electron diffusion inside substrate and random distribution of seeding points over the rutile surface.

It is noteworthy that the absorption coefficient of the solution is almost unchanged when the excitation wavelength is tuned out of the fundamental TiO_2 absorption band within the (400~428) nm range. The absence of recorded Pt pattern proofs that direct Pt reduction from solution was not important at our experimental conditions. Also, no Pt pattern was produced, when sapphire substrates, which posses transmission spectra similar to fused silica, were used. It was checked in wide range of excitation powers 0.07~1.82 mW at the all same other experimental conditions. This observation rules out direct Pt reduction from solution by one or two photon absorption of $PtCl_4^{2-}$ in the solution or the solution itself. Such Pt reduction mechanism, however, should be addressed when either $PtCl_4^{2-}$ concentration or excitation power is increased. For example, at the 100 μW excitation power and the 20 mmol/dm³ concentration of H_2PtCl_6 the number of photons per one $PtCl_4^{2-}$ ion reaches 1.3 in pre-surface area of few tenths of nanometers while the average is only 1×10^{-4} for the all pulse occupied area of the solution.

The time dependence of Pt island growth when the sample is not moving is presented on Figure 3. It was observed that the pattern growth simultaneously starts over the region more extended than illuminated one. The shape of Pt islands is cone-like with base to height ratio of approximately 6:1. The diameter of the Pt pattern is exceeding few times the waist of excitation beam $w = (4\lambda_{ex}/\pi)\cdot F_\#$ ≈ 140 nm, where λ_{ex} is the excitation wavelength, $F_\#$ is the F number of the objective lens defined by

its numerical aperture. High divergence of the beam is responsible for the Pt pattern spreading over the lager area than the irradiation beam waist; e.g. the diameter of the excitation beam is doubled at 70 nm depth inside substrate. Taking into account TiO_2 electron mobility of $\mu_e = 0.16\ cm^2/Vs$,[8] distance of 60 nm is covered by diffusion in time between two adjacent excitation pulses of 12 ns. Such carriers arriving to the surface are a source for $PtCl_4^{2-}$ reduction on more extended area than beam waist itself.

On the early growth stages both the width and the height are following $t^{1/2}$ time dependency. This implies diffusional spreading of the Pt island (solid lines in Figure 3) while at later evolution both dimensions are better fitted by saturable growth (dashed lines). Also, in the case of moving stage, the dimensions of the Pt pattern were found to increase sub-linear (the slope ≤ 1 in log-log presentation) on the incident power with the saturation starting approximately at 600 μW, as it would be expected for one photon absorption of TiO_2. Such behavior, most probably, is related to increasing light scattering and absorption of partially Pt plated surface and lateral spreading of Pt over surface when the irradiated power or irradiation time (Figure 3) are increased. These reasons are diminishing the number of excited carriers in a pre-surface area of TiO_2 available for Pt island formation. For the highest excitation densities employed of few hundreds of μW, the nonlinear recombination should be considered as additional source of intensity dependent saturation, since non-equilibrium carrier density is exceeding $10^{19}\ cm^{-3}$.

The proper choice of Pt ion concentration, stage velocity, the magnification and NA of the objective lens should be made according to certain requirements of Pt patterns to be made. Similar tasks of surface patterning by metals are usually accomplished by photolithographic methods,[5] more complex than presented here. The usage of short femtosecond excitation pulses is not limiting feature for described fabrication procedure to be employed.

In conclusion, we have shown the possibility to fabricate well-defined Pt patterns of submicrometer dimensions by photocatalytic reduction of $PtCl_4^{2-}$.
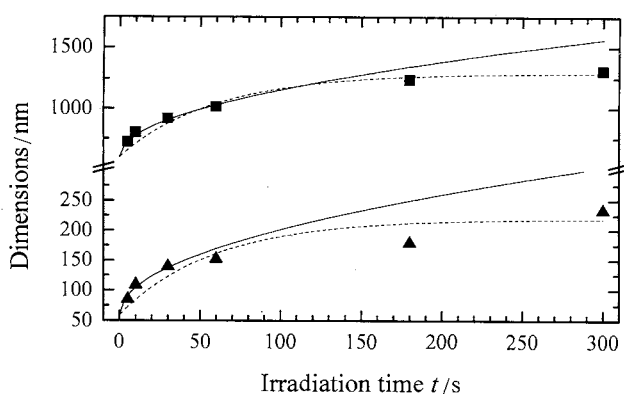
Figure 3. The dependence of Pt island width (■) and height (▲) growth on irradiation time at excitation wavelength of 380 nm and laser power of 152 μW.
Best-fit functions are plotted for diffusional pattern spreading (solid lines) and saturable growth models (dashed lines).

References and Notes

†† On leave from Vilnius University, Sauletekio 10, 2040 Vilnius, Lithuania.
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