Photocatalytic machining of organic molecular layer on a Si wafer surface by use of a porous TiO$_2$ micro wire

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Photocatalytic machining of the organic molecular layer of octadecyl-trichlorosilane (OTS) coated on a Si wafer was investigated in the atmosphere by use of a porous TiO$_2$ micro wire which was prepared by phase separation and selective leaching process. The OTS coated on the Si wafer surface was clearly machined within 1 min under UV irradiation. From the examination of the effect of humidity on the OTS machining rate, the ambient air was found to have sufficient condition for this machining procedure. On the contrary, the OTS in UV non-irradiated area was not machined at all. This indicated "double excitation mechanism", which the photo induced oxygen radicals on TiO$_2$ were further photo excited by the irradiation of UV light, proceeded. This process is capable of on-demand machining of organic molecular layer in normal atmospheric condition.

Key-words: Photocatalyst, Machining, TiO$_2$, OTS, On-demand

1. Introduction

In recent years, a self-assembled monolayer (SAM) has been widely studied for the fabrication of various functional materials. A lithography of SAM was realized by irradiation with deep ultraviolet (DUV) light, and such patterning of SAM have widely investigated in various fields such as patterning of aluminum oxide and tin oxide colloidal suspensions, a site-selective deposition of anatase TiO$_2$ thin film, which applied to a chemical sensor array and a pH sensitive probe, etc. Among those works, Tatsuma et al. have reported that enzymes and algal cell were patterned on gold surface by photocatalytic lithography using a TiO$_2$-coated photomask on the basis of the super-hydrophobic/super-hydrophilic patterns.

Recently, we have reported that the photocatalytically active porous TiO$_2$ micro wire was prepared by use of two-liquid phase separation in TiO$_2$-SiO$_2$ system and subsequent selective leaching process. We have also reported that we succeeded in photocatalytic machining of the surfaces of various polyimide thin films and polymethylmethacrylate (PMMA) by use of the porous TiO$_2$ micro wire under UV light irradiation in the atmosphere. This "photocatalytic machining" technique has various advantages as follows: this process requires no special conditions and equipments such as an ultra high vacuum atmosphere, an electron beam and a laser one. Additionally, this technique causes very little damage to a target substrate because it can use UV light of relatively longer wavelength than 350 nm. Furthermore, this machining process by use of the porous TiO$_2$ micro wire requires no photo-mask and photo-resist. This means that an on-demand machining is able to perform at the arbitrary point of the materials by scanning the micro wire under UV irradiation.

Octadecyltrichlorosilane (OTS) is one of typical organic molecules which can form SAM on various substrates. Therefore, in this study, a organic molecular layer of OTS was formed on a Si wafer surface. The OTS was photocatalytically decomposed by use of the porous TiO$_2$ micro wire under various conditions, and we examined the effects of a UV irradiation time and an angle under various humidity conditions in the atmosphere. In addition to these examinations, the performance of the porous TiO$_2$ micro wire was compared with that of TiO$_2$ thin film coated on a glass rod.

2. Experimental

2.1 Preparation of porous TiO$_2$ micro wire

The TiO$_2$ micro wires were prepared by quenching of a high temperature two-liquid phase separated melt in TiO$_2$-SiO$_2$ system with elongation. The starting composition of the micro wire was 35TiO$_2$-65SiO$_2$+5Al$_2$O$_3$ (mass%). Al$_2$O$_3$ was added in order to form fine and uniform-size TiO$_2$-rich particles in the SiO$_2$-rich matrix, because Al$_2$O$_3$ generally suppresses phase separation in silicate systems. The porous TiO$_2$ micro wire was prepared by selective leaching of a SiO$_2$-rich phase using NaOH aqueous solution. The detail of the sample preparation procedure was reported previously.

2.2 Preparation of TiO$_2$ thin film coated glass rod

The TiO$_2$ precursor solution (Ti concentration = 1 mass%) was prepared by mixing and stirring reagent grade titanium diisopropoxide bis(acetylacetonate), (75 mass% in 2-propanol, Aldrich) and 2-propanol (Wako Pure Chemical) in ambient condition for 1 h. A TiO$_2$ thin film was coated on a silica glass rod of 2 mm in diameter which was cleaned in acetone with ultrasonication. The rod was immersed into the coating solution using a dip-coater and then pulled up at the rate of 1 mm/sec. After the dip coating, the rod was dried at room temperature for 5 min, and calcined at 673 K for 10 min. This coating process was repeated 6 times,
and finally the rod was heat-treated at 773 K for 24 h.

2.3 Preparation of OTS layer
A Si single crystal wafer and a commercial sheet glass plate were used as substrates. A polished p-type Si (100) wafer (Shin-Etsu Chemical Co.) was cleaned in acetone and ethanol, and immersed in an aqueous solution of NH$_3$:H$_2$O:H$_2$O=1:1:21.3 (volume ratio) for 10 min. A sheet glass plate was also cleaned in acetone and ethanol, and soaked in 1 mol/L NaOH aqueous solution for 1 h. Both substrates were rinsed in deionized water and dried in N$_2$ atmosphere. The organic molecular layer of OTS was formed on a substrate by immersing in a 5 mmol/L OTS (Kanto Chemical Co., 95%) solution of toluene at room temperature for 5 min. The substrate was rinsed with toluene to remove unconnected OTS on its surface. Under ambient condition, the sample was dried in an oven at 393 K for 10 min and then cleaned by an ultrasonic bath with ethanol.

2.4 Photocatalytic machining of the OTS layer
The photocatalytic partial machining of the OTS-coated substrate was performed in the atmosphere at room temperature. The porous TiO$_2$ micro wire was set near the surface of the OTS-coated substrate with a distance of 10 or 100 μm, as schematically illustrated in Fig. 1. A Hg–Xe lamp (Kenko, UVF-205S; λ = 365 nm, < 300 mW·cm$^{-2}$) and a LED lamp (Omron, ZUV-C10; λ = 365 nm, ≈1200 mW·cm$^{-2}$) were used as an UV light source. The UV light was irradiated to the OTS-coated surface from the upper side at an angle of 45° or 90°. The machining conditions such as a UV irradiation time and a distance between the wire and the substrate were changed in the experiment. The UV irradiated surfaces were observed by use of a digital camera (Nikon, COOLPIX990) after subjecting to water vapor. A water contact angle on the machined surface was also observed by use of the digital camera with a macro lens.

3. Results and discussion
Figure 2 shows the machined surface of the OTS-coated substrate by use of the non-porous TiO$_2$ micro wire prepared without the selective leaching process (A) and the porous one (B) after Hg–Xe lamp irradiation with an angle of 45° for 30 min. In Fig. 2(B), the OTS was observed clearly to be machined along the shape of the porous wire because the machined surface became hydrophilic. On the contrary, the OTS was machined very slightly as shown in Fig. 2(A) when the non-porous wire was used. These results indicate that the photocatalytic activity of the porous wire was improved since TiO$_2$ phase appeared on the surface of the wire by selective leaching of SiO$_2$-rich phase. Figures 3(A) and (B) show the water contact angle on the OTS-coated substrate and the machined one, respectively. After machining, the surface of the substrate was changed from hydrophobic condition to hydrophilic one, thus, the contact angle became small; 5° or less. These results suggest that the OTS on the machined area was decomposed by photocatalytic oxidation due to TiO$_2$ based on the surface of the micro wire.

Figure 4(A) shows the surface change of the machining area with UV irradiation time by use of the Hg–Xe lamp at an angle of 45°. As the UV irradiation time became long, the machined area gradually became wide. On the left side of the each hydrophilic area where was the opposite side of the UV irradiation to the micro wire, the boundary looked very clear between the machined and the non-machined area compared with that of the right side. Figure 4(B) shows the machined area when the TiO$_2$ thin film coated glass rod was used under the same condition of UV irradiation. The boundary looked unclear compared with that in Fig. 4(A). Especially, the OTS was hardly decomposed by the UV irradiation for 1 min. It was confirmed that the photocatalytic activity of the porous TiO$_2$ wire was higher than that of the TiO$_2$ thin film coated glass rod. Since the hydrophilic area was also clear within 1 min in Fig. 4(A), this machining process by use of a porous TiO$_2$ micro wire may become a candidate for a novel on-demand machining under normal atmospheric condition.

Figure 5 shows the change of the width of the machined area of the OTS-coated surface with the irradiation time of
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The effect of the humidity in the atmosphere on the machining of the OTS was also examined. The UV light from LED was irradiated on the wire at an angle of 45° for 30 min under various humidity conditions (16%, 46% and 78%). In 46% and 78%, the similar results of the machining of OTS shown in Fig. 4(A) were obtained. However, any hydrophilic area on the OTS-coated surface was not observed in the condition of 16%. These results indicate the one of key points of this procedure that the decomposition of the OTS by the porous TiO2 micro wire requires certain humidity during machining. In other words, the humidity of the normal atmospheric condition is sufficient for this machining procedure considering from the result of 46% in humidity. This is a great advantage of this machining procedure because the humidity control is unnecessary during machining.

From the above mentioned results, we considered the mechanism of the photocatalytic machining of OTS by use of the porous TiO2 micro wire. As the UV irradiation time was long and the distance between the wire and the substrate was long, the machining area was spread significantly. These results strongly indicate that the diffusion of reactive oxygen species such as ·OH was involved in the decomposition of the OTS. In addition, the OTS machining was able to proceed under 46% and 78% humidity. In the photocatalytic decomposition of organic polymer substrates by use of TiO2, it was reported that H2O molecule in the atmosphere induces oxygen radicals as following reaction:

\[ H_2O(aq) + h^+ \rightarrow \cdot OH + H^+ \]

In spite of the UV light irradiation for 120 min vertically, the OTS-coated surface just under the wire, where was in shadow of the UV light, did not become hydrophilic. From this result, we considered that the photo excitation of OTS in itself or Si substrate by UV light make the photocatalytic decomposition of OTS proceed, or that the reported "double excitation mechanism", which the photo induced oxygen radicals on TiO2 were further photo excited by the irradiation of UV light, needs to involve OTS machining. However, the OTS was reported not to be excited by a Hg–Xe lamp. Additionally, the decomposition of OTS coated on the sheet glass was in the same manner as that of OTS coated on the Si wafer. These results suggest that this photocatalytic machining proceeds owing to the "double excitation mechanism".
4. Conclusion

The photocatalytic machining of the OTS-coated substrate was successfully performed by use of the porous TiO₂ micro wire under normal atmospheric condition. This machining process probably involves "double excitation mechanism". Therefore, this procedure needs to irradiate UV light not only the porous TiO₂ micro wire but the surface of the OTS-coated substrate to make it machine. As a result of the effect of the humidity in the atmosphere, the OTS machining was also observed in the ambient atmosphere, that is, the humidity control is unnecessary for this machining process. Additionally, this process proceeded relatively fast so that it was realized within 1 min at least. Therefore, this "photocatalytic machining" technique is considered to have a potential for the development of a micro-nano scaled patterning of an oxide thin film on various substrates. In particular, this machining process by use of "porous TiO₂ micro wire" may become a candidate for a novel on-demand machining under normal atmospheric condition.

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