

Patterning of TiO₂ Thin Film on UV Irradiated Organic Polymer Substrates

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TiO₂ has major interest for its wide variety of functions such as photocatalyst, hydrophilic coating, electrode of photovoltaic cells, bioactive coating and so on. It is considered that patterning of TiO₂ thin film will enable the development of advanced devices utilizing these functions. Polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) were used as substrates. A photomask was placed on the substrates and UV rays were irradiated. After UV irradiation, polar groups such as -OH and -COOH were detected on the surface of PS, PMMA and PVC substrates by FT-IR measurement. The substrates were soaked in (NH₄)₂TiF₆ and B₂O₃ mixed aqueous solution for 4 h at 40°C. TiO₂ thin film was formed on whole the surface of the substrates. Scotch® tape was put on the film and peeled off. The TiO₂ thin film formed on the UV irradiated region of the substrate remained. It is considered that polar groups introduced by the UV irradiation increased the adhesive strength of TiO₂ thin film to the substrate. TiO₂ pattern clearly transcribing that of photomask was formed.

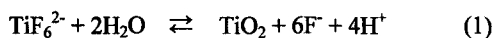
Key words: UV, TiO₂, Polar group, Patterning, Organic polymer, Aqueous solution

1. INTRODUCTION

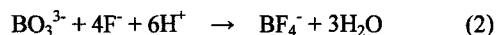
TiO₂ has major interest for its wide variety of functions such as photocatalyst [1] hydrophilic coating [2] electrode of photovoltaic cells [3], bioactive coating [4], insulator for electronic devices [5], photonic crystal [6] and so on. It is considered that patterning of TiO₂ thin film will enable the development of advanced devices utilizing these functions.

Usually, TiO₂ thin film was prepared by sol-gel process [7] or vapor phase process such as chemical vapor deposition [8], sputtering [9], and so on. However, these methods have several disadvantages. Sol-gel process and chemical vapor deposition require heating, which is injurious because of possibility of a change in the shape and/or size of the film and of crack formation, and are not applicable for low heat resistant substrates such as organic polymers. For sputtering, expensive vacuum equipments are required and the film areas are restricted.

Recently, we have presented methods for forming oxide ceramics from aqueous solution [10-12]. TiO₂ can be formed from aqueous solution at ordinary temperature and ordinary pressure by hydrolysis reaction of titanium fluoro-complex [13]. This method is advantageous because no vacuum, no high temperature or no expensive apparatus will be required, and substrates, even those with wide areas and/or complicated shapes, are available. The reaction is considered as follows. The chemical equilibrium between hexafluorotitanate ion and TiO₂ holds as in reaction (1).



When borate ion is added, fluoride ion is consumed by reaction (2).



Then the chemical equilibrium in reaction (1) is shifted from left to right in order to increase fluoride ions, resulting in the formation of TiO₂.

It was reported that surface modifications of organic polymers with NaOH solution [14], HCl solution [15], glow-discharge [16] or UV irradiation [17] effectively improved adhesive strength of apatite thin film due to formation of polar groups on the surface of the substrate. We have considered that adhesive strength of TiO₂ thin film can also be improved by the similar surface modifications of organic polymer mentioned above. It is expected that when UV is irradiated through a photomask, patterned regions with high and low adhesive strength to TiO₂ can be formed on the surface of organic polymer substrates.

In the present study, UV rays were irradiated on organic polymer substrates through photomask, and TiO₂ thin film was formed on the substrates, then the TiO₂ thin film was peeled off. Patterning of TiO₂ thin film utilizing the difference of adhesive strength to the substrate was investigated.

2. EXPERIMENTAL

2.1 UV irradiation

Polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) cut to 10×15×1 mm³ in size were used as substrates. A photomask was put on the substrate and UV rays of 253.7 or 365 nm in wavelength were irradiated. The illumination of UV lamp was 190 μW·cm⁻² or 750 μW·cm⁻², respectively. The distance between UV lamp and substrate was set to 10 cm.

2.2 Formation of TiO₂ pattern

The substrate UV irradiated through a photomask was

suspended in a mixed solution of $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 in an incubator at 40°C for 4 h. The concentration of $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 was $31.3 \text{ mmol}\cdot\text{dm}^{-3}$ and $203 \text{ mmol}\cdot\text{dm}^{-3}$, respectively. It is expected that TiO_2 thin film is formed on the entire surface of the substrate. Scotch® tape was put on the TiO_2 thin film and peeled off.

2.3 Analysis

The UV irradiated surface of the substrate was analyzed by Fourier-transform infrared attenuated total reflection (FTIR-ATR: FT/IR 420, JASCO, Japan). Formation of TiO_2 thin film was confirmed by thin film X-ray diffraction (TF-XRD: Rint 2500, Rigaku, Japan) and scanning electron microscopy (SEM: ESEM-2700, Nikon, Japan). The thickness of the thin film was measured by atomic force microscopy (AFM; Nanoscope III, Digital Instruments, USA). The surface of the substrate after putting Scotch® tape on and peeling off was observed by a CCD scanner (MultiReader1200U, NEC. Co, Japan).

3. RESULTS AND DISCUSSION

3.1 Surface modification by UV irradiation

Figure 1 shows FTIR-ATR spectra of the surface of PS, PMMA, PVC substrates 253.7 nm UV irradiated for various periods. For PS, peaks attributed to carboxyl group $-\text{COOH}$ and hydroxyl group $-\text{OH}$ were observed after UV irradiation for over 2 h. For PMMA and PVC, similar peaks were observed after over 48 h. It is indicated that polar hydrophilic groups such as $-\text{COOH}$ and $-\text{OH}$ were formed on the surface of the polymer substrates by photooxygenation [17, 18]. In the case of 365 nm UV, no peak attributed to carboxyl group or

hydroxyl group was observed even after 24 h irradiation on any substrate. The binding energy of C-H bond is 4.29 eV [19], which corresponds to 289 nm in wavelength. It is considered that the energy of 365 nm UV is deficient in breaking C-H bond and no photooxygenation proceeded.

3.2 Formation of TiO_2 thin film

After soaking in the $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution, formation of thin film on the entire surface was observed by naked eye. Figure 2 shows TF-XRD patterns of the surface of PS, PMMA and PVC substrates before and after soaking in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h. For all the organic polymer substrates, XRD peaks attributed to anatase type TiO_2 were observed. Figure 3 shows SEM micrograph of the surface of PS substrate soaked in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h. It was observed that uniform and dense TiO_2 thin film was formed on the surface of the substrate. Similar thin film formation was also observed for PMMA and PVC substrate. The thickness of the thin film was measured as $\sim 160 \text{ nm}$ by AFM. The film thickness is very thin and this will explain that only weak peaks were observed by XRD [13].

3.3 Formation of TiO_2 pattern

Figure 4 shows scanned images of the surface of PS, PMMA and PVC substrates, 253.7 nm UV irradiated through a photomask for 2, 4 or 12 h, soaked in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h, and then Scotch® tape put on, peeled off. In the case of PS substrate, TiO_2 thin film pattern transcribing the UV irradiated region was clearly formed on the substrate by UV irradiation for 2 h or longer. It is considered that

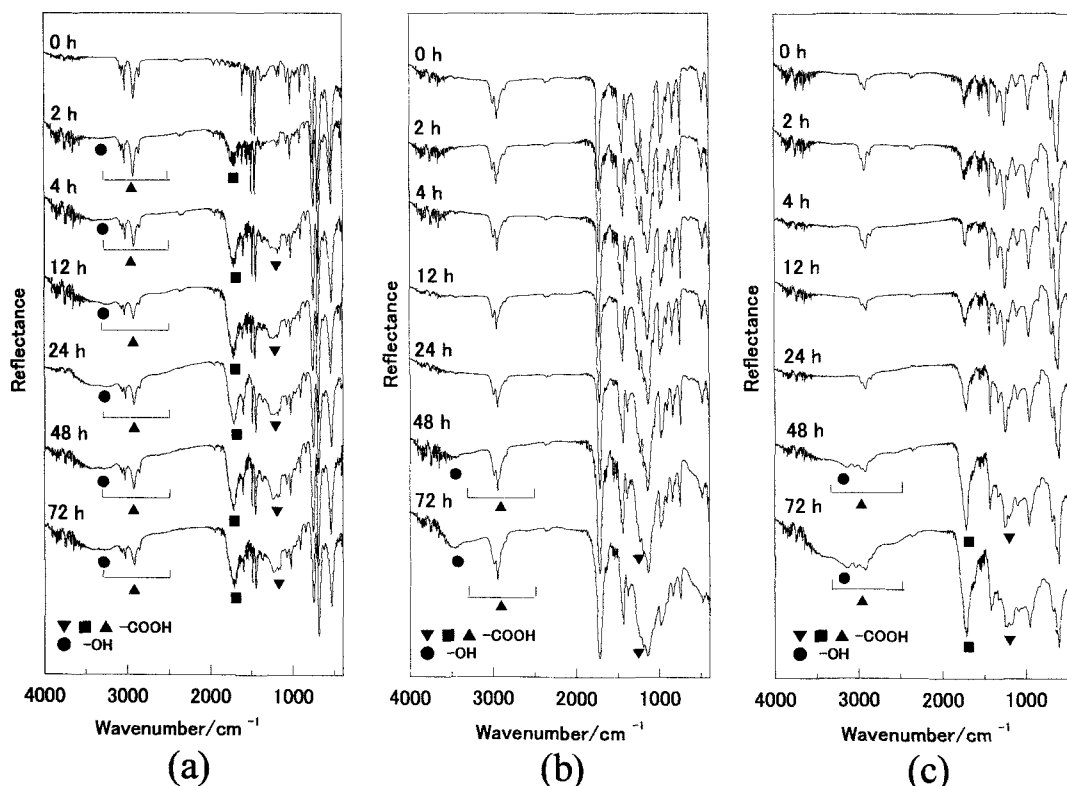


Fig. 1 FTIR-ATR spectra of the surface of (a) PS, (b) PMMA, (c) PVC substrates 253.7 nm UV irradiated for various periods.

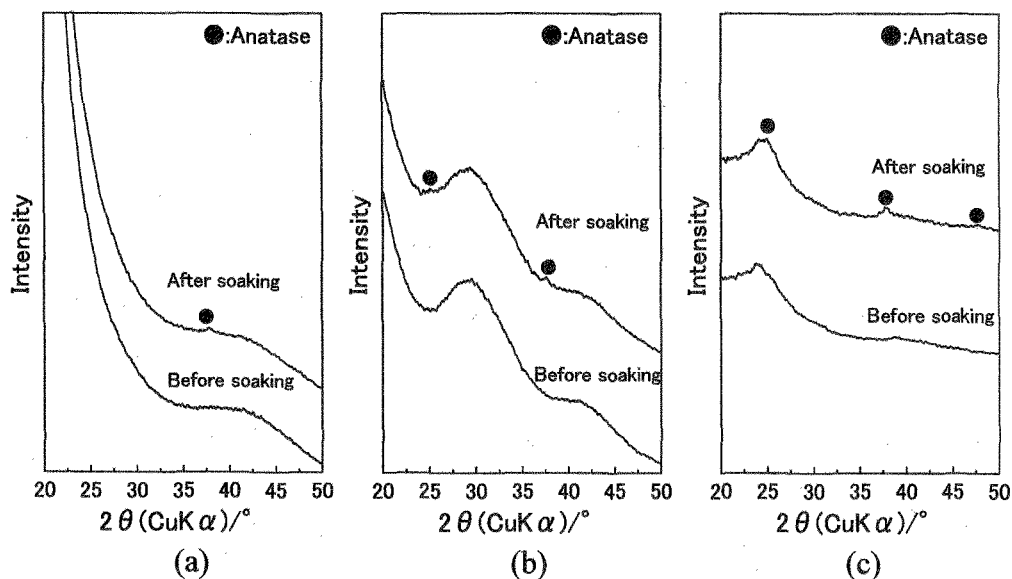


Fig. 2 TF-XRD patterns of the surface of (a) PS, (b) PMMA and (c) PVC substrates before and after soak in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h.

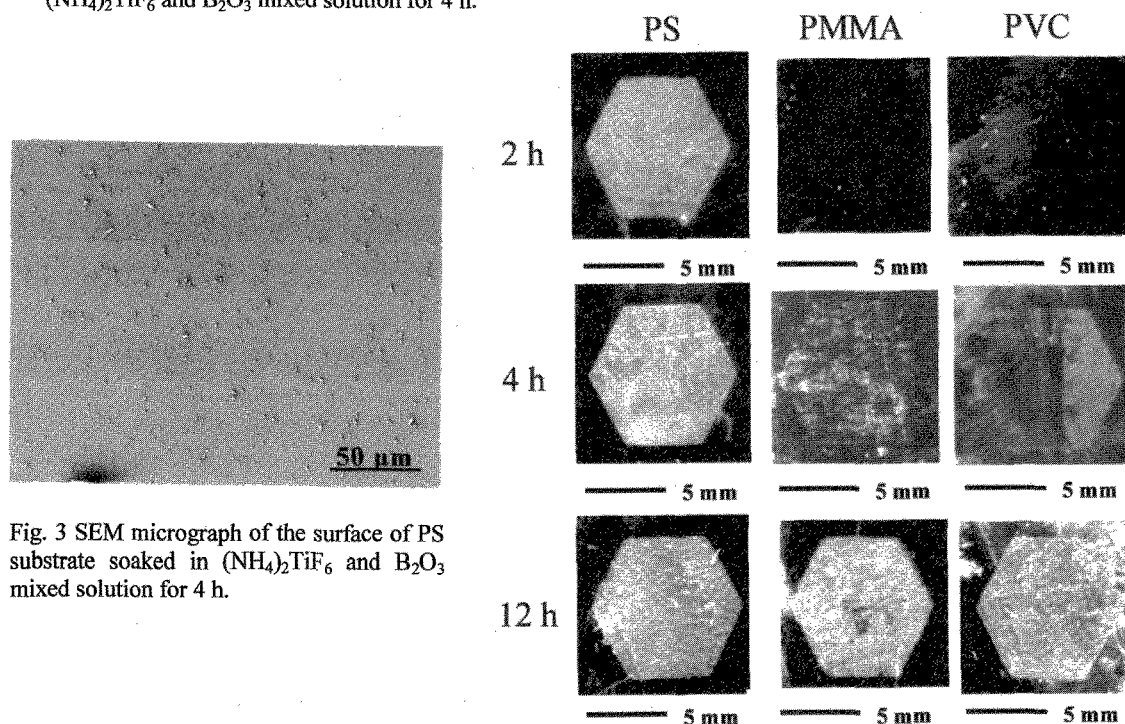


Fig. 3 SEM micrograph of the surface of PS substrate soaked in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h.

Fig. 4 Scanned images of the surface of PS, PMMA and PVC substrates after 253.7 nm UV irradiation through a photomask for 2, 4 or 12 h, soaking in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed solution for 4 h and then putting Scotch® tape on and peeling off.

polar groups such as $-\text{COOH}$ and $-\text{OH}$ introduced by the UV irradiation increased the adhesive strength of TiO_2 thin film to the substrate. The boundary of the pattern was straight and distinct. For PMMA, clear pattern was obtained for 12 h irradiation. For PVC, clear pattern was not obtained even for 12 h irradiation. This result is very compatible with the FTIR-ATR measurement that polar groups were formed on PS with UV irradiation for shorter period than on PMMA and PVC.

In the case of 365 nm UV, no TiO_2 thin film pattern

was obtained. This is very consistent with the result of FTIR-ATR measurement that no peak attributed to carboxyl group or hydroxyl group was observed.

Figure 5 shows scanned images of TiO_2 patterns formed on PS substrate 253.7 nm UV irradiated for 12 h. Various kinds of patterns such as a circle, a double allow shape and a balloon-like shape were formed clearly by TiO_2 thin film on the PS substrate. Figure 6 shows scanned images of TiO_2 patterns with various shapes formed on PMMA substrate 253.7 nm UV irradiated for 12 h. Various patterns such as a block, an arrow

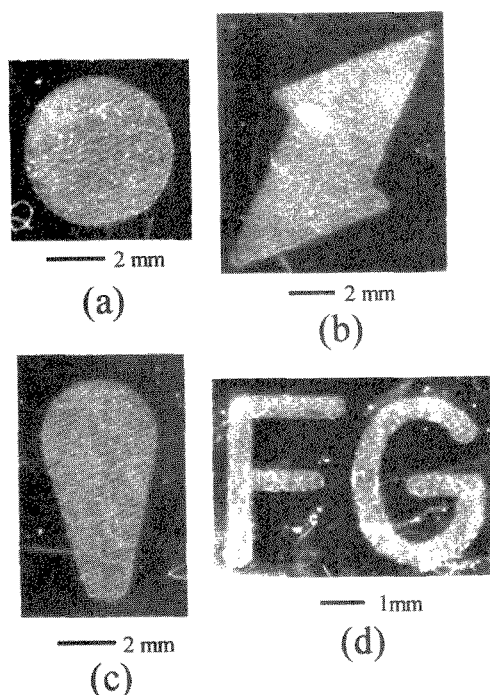


Fig. 5 Scanned images of TiO_2 patterns with various shapes formed on PS substrate 253.7 nm UV irradiated for 12 h.

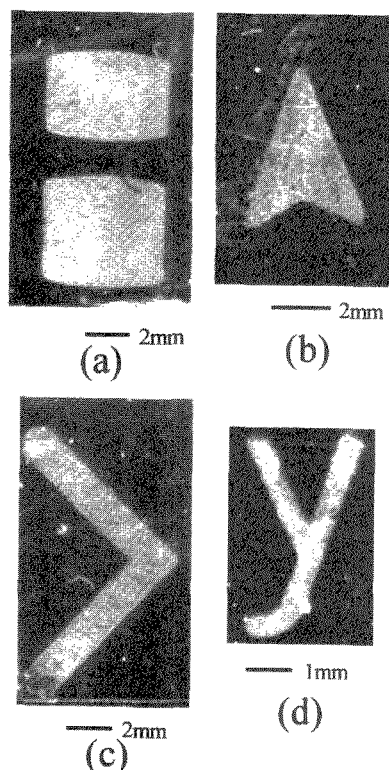


Fig. 6 Scanned images of TiO_2 patterns with various shapes formed on PMMA substrate 253.7 nm UV irradiated for 12 h.

and a bending line were distinctly formed by TiO_2 thin film. For both substrates, corner of the bending line was

clearly outlined and characters of 0.6 mm in width were finely formed by TiO_2 thin film.

4. CONCLUSIONS

UV rays were irradiated on the surface of PS, PMMA and PVC substrates through a photomask. By 253.7 nm UV irradiation, polar groups such as $-\text{OH}$ and $-\text{COOH}$ were formed on the surface of substrates. The substrates were soaked in $(\text{NH}_4)_2\text{TiF}_6$ and B_2O_3 mixed aqueous solution and TiO_2 thin film was formed on the entire surface of the substrates. Scotch® tape was put on the film and peeled off. The TiO_2 thin film formed on the UV irradiated region of the substrate remained and TiO_2 thin film pattern transcribing the UV irradiated region was clearly formed on the substrate.

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