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# Nanostructured polysilane–titania hybrids and their application to porous titania thin films

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## Abstract

We have prepared polysilane–titania hybrid thin films using titanium alkoxides with poly(methylphenylsilane)/3-methacryloxypropyltriethoxysilane block copolymer (P(MPS-*co*-MPTES)) via sol–gel reaction. The polysilane block copolymer bonded to titania component through Si–O–Ti derived from hydrolysis/condensation of P(MPS-*co*-MPTES) and Ti(O-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>. Additionally, it was found by tapping-mode atomic force microscope (AFM) that the polysilane segments disperse in titania component in a range of several 10 nm. The polysilane–titania hybrid thin films have been applied to prepare nanoporous titania thin films.

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**Keywords:** Polysilane; Titanium oxide; Organic–inorganic hybrid; Nanostructures; Atomic force microscope

## 1. Introduction

Organic–inorganic hybrids are performed by dispersion of organic and inorganic components through various chemical bonds [1,2]. Especially, the hybrids prepared from mixture of organic and inorganic component in nano level or molecular level have been thought to be promising materials in a field of electronics or photonics [3]. We have also prepared various polysilane–silica hybrid thin films from polysilane–acrylic or polysilane–methacrylic block copolymers with alkoxyethyl or amide groups via sol–gel reaction using tetraethoxy orthosilicate (TEOS) [4–9]. The polysilane–silica hybrid thin films, in which polysilane block was mixed with the silica component through covalent or hydrogen bonding, had various interesting functionalities [4,8]. For example, the polysilane–silica hybrids had controllable refractive indices according to the feed ratio of polysilane/silica [9]. Furthermore, they had a

continuous refractive index change ( $\Delta n \geq 0.1$ ) dependent on a degree of photolysis of polysilane segments by UV irradiation.

We have also prepared homogeneous polysilane–titania hybrid thin films using titanium ethoxide (Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) modified with acetylacetone (Acac) [10,11], in which titania is well-known as photo-functional materials, i.e. photocatalyst and photochemical solar cell [12,13]. It was found that these polysilane–titania hybrid thin films had numerous unevenness at a few hundred nanometer intervals to generate mesoporous TiO<sub>2</sub> thin films after UV irradiation. In this report, polysilane–titania hybrid thin films were prepared using Ti(O-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> without Acac modification and these structures were examined by using various spectroscopic and microscopic measurements.

## 2. Experimental

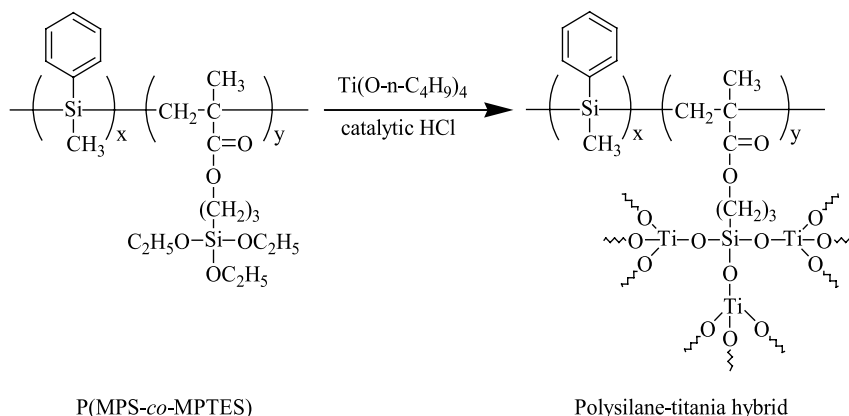
The polysilane block copolymer, P(MPS-*co*-MPTES), has been prepared from photopolymerization of 3-methacryloxypropyltriethoxysilane (MPTES) with

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poly(methylphenylsilane) (PMPS) as a macro-photo-initiator according to our previous report [4]. The structure of P(MPS-*co*-MPTES) was as following:  $M_n = 1.31 \times 10^4$ ,  $M_w/M_n = 1.83$ ;  $x = 139$ ,  $y = 24$  (in Scheme 1, calculated from the result of  $^1\text{H-NMR}$  spectrum);  $\lambda_{\text{max}} = 338.4$  nm. The sol-gel reaction for preparation of hybrid thin films was as described below. P(MPS-*co*-MPTES) (30 mg, containing 0.03 mmol of MPTES) was dissolved in distilled tetrahydrofuran (THF) (1.0 ml) with catalytic amount of HCl (ca. 1 ppm) and stirred for 1 h.  $\text{Ti}(\text{O-}n\text{-C}_4\text{H}_9)_4$  (Gelest, Inc.) ( $10 \times n$  mg,  $n = 1, 3, \text{ and } 9$ , which were 0.03, 0.09, and 0.27 mmol, respectively) dissolved in distilled THF (1.0 ml) was added to the above THF solution. After stirring the solution for 1 h and filtering through a 0.2  $\mu\text{m}$  PTFE membrane, this solution (sol) was spin-coated on the silicon or silica substrate, followed by aging the hybrid thin film at 120  $^\circ\text{C}$  for 1 h in air. Hereinafter, the polysilane-titania hybrids were classified by the calculated feed ratios of P(MPS-*co*-MPTES) (25, 50, and 75 wt.%). Furthermore, we have prepared a thin film from P(MPS-*co*-MPTES) and  $\text{Ti}(\text{O-}n\text{-C}_4\text{H}_9)_4$  without catalytic HCl. UV irradiation to the polysilane-titania hybrid thin films was performed using a USHIO SP-V with a light intensity of 110  $\text{mW cm}^{-2}$  for 10 s.

FT-IR spectra were recorded using a Nicolet Impact 400. UV-vis absorption spectra were examined by a Hitachi U-3210. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 with an excitation wavelength of 320 nm. X-ray photoelectron spectroscopy (XPS) was carried out with a ULVAC Phi ESCA 5700 to confirm the photolysis of polysilane segments. Ellipsometry measurements were performed using a ULVAC ESM-1 with a He-Ne laser. Tapping-mode atomic force microscope (AFM) measurements were conducted using a Digital Instruments Nanoscope IIIa with a tip fabricated from silicon (length: 125  $\mu\text{m}$ , resonant frequency: 200–400 kHz, and tip radius: 5–20 nm).



Scheme 1.

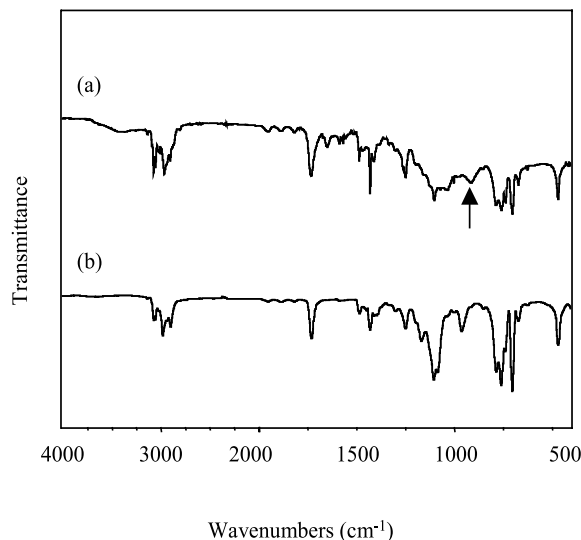


Fig. 1. FT-IR spectra of (a) a polysilane-titania hybrid thin film containing 75 wt.% of P(MPS-*co*-MPTES) and (b) a thin film of P(MPS-*co*-MPTES). The arrow shows an absorption peak at 922  $\text{cm}^{-1}$  due to Si-O-Ti bond.

### 3. Results and discussion

As mentioned in our previous report,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  was used for the sol-gel reaction with Acac to stabilize the sols, because of its rapid hydrolysis/condensation [10]. However, we have successfully prepared homogeneous thin films of polysilane-titania hybrids using  $\text{Ti}(\text{O-}n\text{-C}_4\text{H}_9)_4$  and catalytic acid without modification by Acac. Moreover, even a large amount of the feed ratio of 75 wt.% of  $\text{Ti}(\text{O-}n\text{-C}_4\text{H}_9)_4$  gave homogeneous thin films of polysilane-titania hybrids. This is possibly due to the slower reactivity of  $\text{Ti}(\text{O-}n\text{-C}_4\text{H}_9)_4$  than that of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ .

The structures of the polysilane-titania hybrid were examined with various measurements. The FT-IR spectra of polysilane-titania hybrids showed retention of the chemical structure of polysilane segments in Fig. 1. In the FT-IR spectrum of Fig. 1(a), some increase of

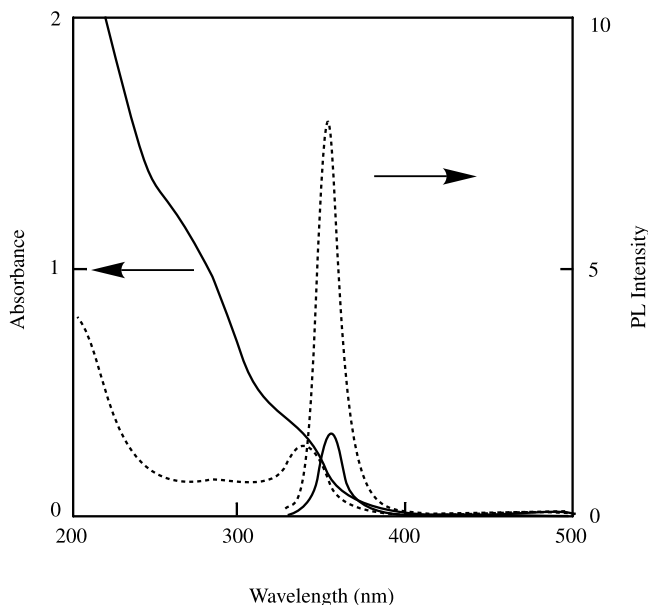


Fig. 2. UV-vis absorption and PL spectra. Straight line indicates the spectra of polysilane-titania hybrid thin films containing 50 wt.% of P(MPS-co-MPTES) and dashed lines the spectra of P(MPS-co-MPTES).

absorption below  $900\text{ cm}^{-1}$  was possibly indicative of the formation of Ti-O-Ti bond. The polysilane-titania hybrid thin film containing 75 wt.% of P(MPS-co-MPTES) had an absorption peak at  $922\text{ cm}^{-1}$  due to Si-O-Ti bond in Fig. 1(a), in analogy with Ref. [14]. Additionally, hydrolysis/condensation of Si-OC<sub>2</sub>H<sub>5</sub> in P(MPS-co-MPTES) was confirmed by the results of the disappearance of absorption peak at  $960\text{ cm}^{-1}$  in Fig. 1(b), which were assigned to a characteristic absorption due to Si-OC<sub>2</sub>H<sub>5</sub> [15]. In the UV-vis absorption spectra of the polysilane-titania hybrid thin films, as shown in

Fig. 2, there was a broad absorption band below 350 nm due to titania component. In addition to the absorption band of titania, a peak around 330 nm due to  $\sigma$ -conjugation of Si-Si main chain was observed. No difference of PL peak around 357 nm excited by 320 nm clarified retention of electronic state of polysilane segment even in the titania component, as shown in Fig. 2. PL intensity of the polysilane-titania hybrid thin film, however, was much smaller than that of P(MPS-co-MPTES). It would be predicted that there is a certain interaction between polysilane segments and titania components. Further details of the PL results will be reported elsewhere.

We have already reported that the polysilane-titania hybrid thin films prepared from Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> modified with Acac gave numerous unevenness around 10–20 nm at a few hundred nanometer intervals by removal of polysilane segments after photolysis [10,11]. Also in this paper, surface morphologies of the polysilane-titania hybrid thin films, which were prepared from Ti(O-*n*-C<sub>4</sub>H<sub>9</sub>) with catalytic HCl, before and after UV irradiation followed by soaking with 2-propanol was observed by using tapping-mode AFM, as shown in Fig. 3. The photolysis of polysilane segments was confirmed by disappearance of UV ( $\sigma$ - $\sigma^*$ ) absorption and Si<sub>2p</sub> peak assigned to Si-Si bond in the XPS spectrum. A thin film prepared without catalytic HCl had a rugged surface after UV irradiation (Fig. 3(a)). On the other hand, the polysilane-titania hybrid thin films prepared with catalytic HCl had numerous pores with several 10 nm (Fig. 3(b)). These results suggest that sol-gel reaction using catalytic HCl gave efficient hydrolysis/condensation enough to leave the fine titania component and the nanoporous surface structure even after soaking with 2-propanol. But it should be noted that the remaining

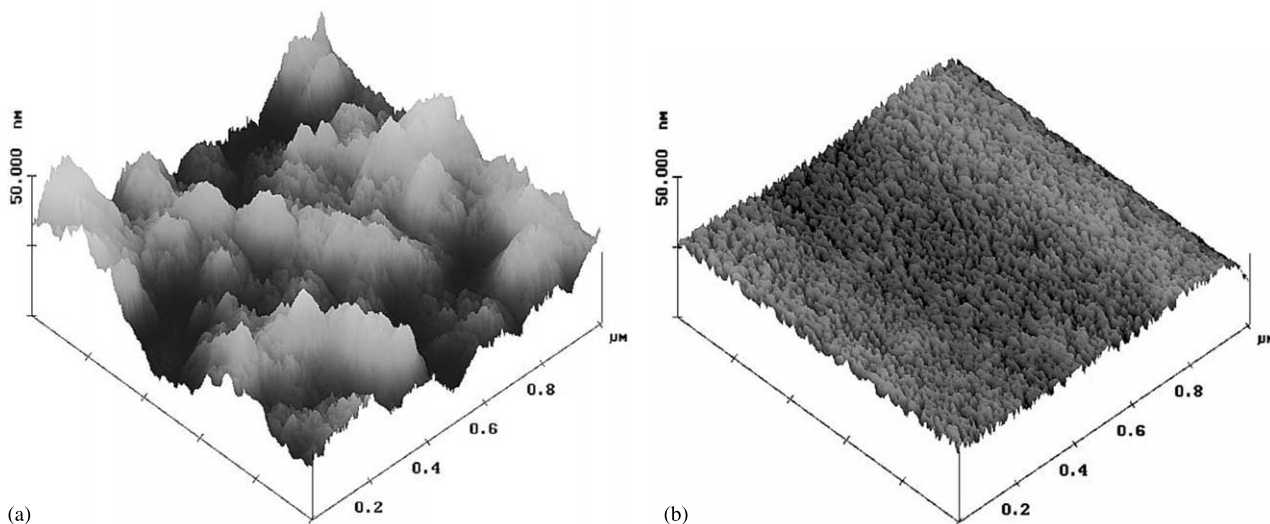


Fig. 3. AFM images ( $1 \times 1\ \mu\text{m}^2$ ) of (a) a thin film prepared from a mixture of P(MPS-co-MPTES) and Ti(O-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> without HCl and (b) polysilane-titania hybrid thin film. Height range is 50 nm. Both films contained 25 wt.% of P(MPS-co-MPTES).

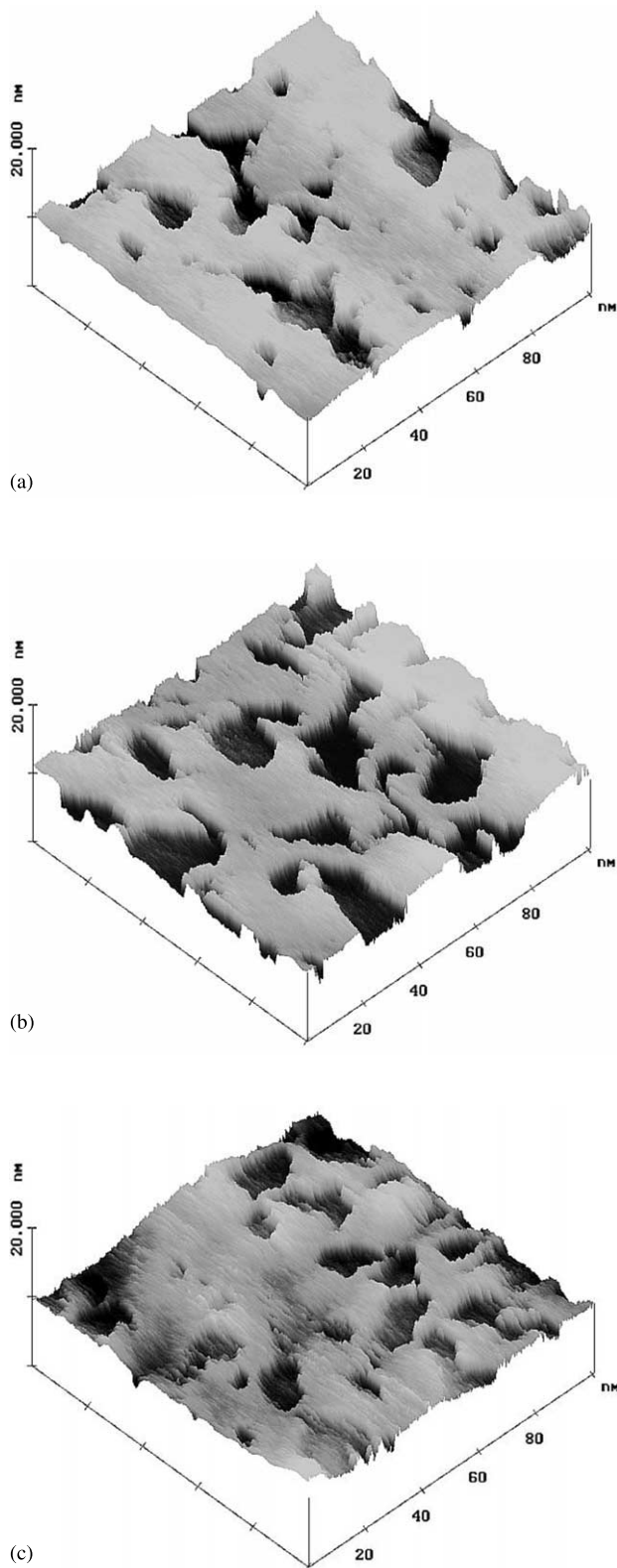


Fig. 4. AFM images ( $100 \times 100 \text{ nm}^2$ ) of polysilane–titania hybrid thin films containing (a) 25, (b) 50, and (c) 75 wt.% of P(MPS-*co*-MPTES). Height range is 20 nm.

titania components did not have a homogeneous structure because the polysilane–titania hybrid thin films was aged at  $120^\circ\text{C}$  in this work, although heat treatment of  $> 500^\circ\text{C}$  is required for the formation of anatase-type  $\text{TiO}_2$  structure. Additionally, it was found that the surface state varied with the feed ratio of P(MPS-*co*-MPTES) as the magnified AFM images in a range of  $100 \times 100 \text{ nm}^2$ , as shown in Fig. 4. The number of pores in the titania thin films increased according to the feed ratio of P(MPS-*co*-MPTES) from 25 to 50 wt.% (Fig. 4(a) and (b)). Furthermore, the surface shape with calm roughness was ascertained in Fig. 4(c), when a large amount of polysilane was removed from the polysilane–titania hybrid containing 75 wt.% of P(MPS-*co*-MPTES). Surface area ratio, which was the percentage of the three-dimensional surface area to two-dimensional surface area ( $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ ) calculated from a roughness analysis of a Digital Instruments NanoScope IIIa software Version 4.10, also indicated the porous structures of the photo-degraded hybrid thin films. The polysilane–titania hybrid thin films before UV irradiation had a surface area ratio less than 1%, but the hybrid thin films containing 25, 50, and 75 wt.% after UV irradiation possessed surface area ratios of 10.0, 10.6, and 5.4%, respectively. These surface area ratios are consistent with tendency of porosity observed by the AFM images of the polysilane–titania hybrid thin films after UV irradiation as described above. The molar ratio of both alkoxy groups,  $\text{OC}_2\text{H}_5/\text{O}-n\text{-C}_4\text{H}_9$ , in polysilane–titania hybrids containing 25, 50, and 75 wt.% of P(MPS-*co*-MPTES) were 0.09/1.056, 0.09/0.352, and 0.09/0.116, respectively. In the case of 75 wt.% hybrid thin films, most of  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$  was consumed for Si–O–Ti bond formation more than Ti–O–Ti, on account of the equimolecular amount of their alkoxy groups. It may be assumed that the incomplete titania component caused the rugged surface of the hybrid thin film from removal of P(MPS-*co*-MPTES) after photolysis of polysilane segments.

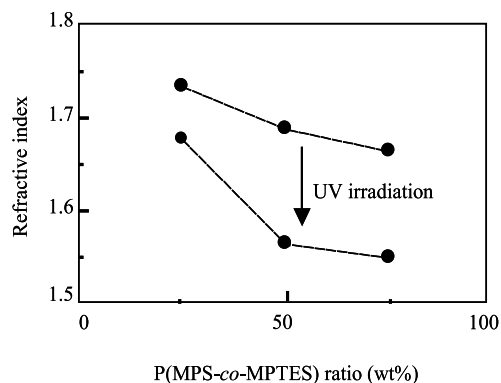


Fig. 5. Refractive index changes of polysilane–titania hybrid thin films containing 25, 50, and 75 wt.% of P(MPS-*co*-MPTES).

The refractive indices of the polysilane–titania hybrid thin films were measured by ellipsometry. The film thickness of the polysilane–titania hybrid thin films was around 100 nm and decreased by less than 30% after UV irradiation, and the refractive indices of each polysilane–titania hybrid thin films significantly changed, as shown in Fig. 5. Regardless of that refractive indices of titania prepared via sol–gel method were higher than that of PMPS, 1.91 and 1.67, respectively, Fig. 5 indicates that the nanoporous structures lowered the value of the polysilane–titania hybrids after UV irradiation. Furthermore, the change of refractive index increased according to the feed ratio of P(MPS-*co*-MPTES) from 25 to 50 wt.%, and the change seems to be saturated at the feed ratio of 75 wt.%. It seemed that this saturation of refractive index change reflects the rugged surface of polysilane–titania hybrid containing 75 wt.% of P(MPS-*co*-MPTES), as shown in Fig. 4(c). Therefore, these results also suggest that the hybrid thin films with higher content of the polysilane block copolymer were deformed to nanostructure by photolysis of polysilane segments.

#### 4. Conclusions

Polysilane–titania hybrid thin films were prepared from P(MPS-*co*-MPTES) and  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$ . It was found that polysilane segments in the polysilane–titania hybrids retained their chemical and electronic properties similar to the non-hybrid polysilane thin film. The AFM images after UV irradiation clarified nanostructured polysilane–titania hybrids, in which polysilane segments dispersed in titania component in a range of several 10 nm. This is due to good miscibility of polysilane block copolymers with titania component through Si–O–Ti bonds formed by efficient hydrolysis/condensation using HCl. The significant refractive index change before and

after UV irradiation supported the nanoporous structure of the polysilane–titania hybrid thin films.

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