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# Effect of silica addition on crystallinity and photo-induced hydrophilicity of titania–silica mixed films prepared by sol–gel process

Masahiko Maeda*, Shinji Yamasaki

*OEDS Research and Development Center, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan*

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**Abstract**

Effect of silicon dioxide (silica) addition into titanium oxide (titania) films on crystallinity and photo-induced hydrophilicity was investigated. Titania films and titania–silica mixed films with 20% or 50% silica were prepared by spin-coating deposition. For the titania films, photo-induced hydrophilicity is only observed in the films with anatase polycrystalline structure. For the titania–silica mixed films, however, despite these films showing no obvious anatase polycrystalline structure, very strong photo-induced hydrophilicity is observed. Particularly, even super-hydrophilicity where the contact angle shows 0° is easily observed for the titania–silica mixed films with 20% silica. The hydrophilicity of the titania films correlates closely with anatase crystalline structure. In the titania–silica mixed films, the synergistic effects of anatase polycrystalline structure of titania and water-trapping effect of silica are important for their strong photo-induced hydrophilicity.


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*Keywords:* Spin-coating; $TiO_2$–$SiO_2$ mixed film; Photocatalyst

## 1. Introduction

Titania–silica-based films have received a great deal of attention on the optical planar waveguides due to their low thermal expansion coefficient, controllability of refractive index, and high thermal stability [1–6]. The performance of the optical planar waveguide, particularly the optical loss, depends on the film structure, so many studies on the structure of the titania–silica mixed films have been performed using various analyses, for example, X-ray diffraction, X-ray photoelectron spectroscopy, transition electron microscopy, atomic force microscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance, and photoluminescence [7–13]. In addition, the titania–silica mixed films have also been considered as attractive materials for photo-induced catalytic applications, particularly photo-induced hydrophilicity. The photo-induced hydrophilicity has been observed firstly on the titanium oxide surface [14]. This phenomenon has been considered, that trapping of adsorbed water at the oxygen defects caused by reduction of $TiO_2$ matrices themselves resulting in the formation of hydrophilic domains [14]. For the titania–silica mixed films, the hydrophilicity of the film surface enhanced by the addition of silica into the titania films and extreme wettability, called super-hydrophilicity, was observed [15,16]. The photo-induced hydrophilicity has received much attention from the standpoint of environmental applications. In spite of its potential into wide application fields, however, the investigation on hydrophilic properties of titania-based films has been less than that on the photo-induced oxidation which is another interesting photo-induced chemical reaction that occurs on the titania-based film surface. Under these circumstances, correlation between the film structure and photo-induced

* Corresponding author. Tel.: +81 762940649; fax: +81 762946711.
*E-mail address:* mmaeda@neptune.kanazawa-it.ac.jp (M. Maeda).

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hydrophilicity of the titania–silica mixed films has not yet been clear.

As regards the preparation of the titania–silica composite films, a number of techniques including electron-beam evaporation [17], chemical vapor deposition [18], flame hydrolysis [19], and sol–gel processes [20–22] have been reported. Among them, sol–gel processes have some advantages such as relative simplicity, low cost, easy controllability of composition of the deposited films, low environmental load, and so on. Therefore, we have adopted the spin-coating deposition in order to prepare the titania–silica mixed films.

In this study, we investigated the effect of silica addition into titania films on crystallinity as well as photo-induced hydrophilic characteristics. The crystalline structure of the films was measured by X-ray diffraction analysis. The hydrophilicity was evaluated by means of contact angle measurement using the water droplet.

## 2. Experimental details

Titania and titania–silica sol–gel solutions were prepared as described in Refs. [23–26]. The preparation procedure involves hydrolysis of tetraisopropoxytitanium and/or tetraethoxysilane. The titania film and titania–silica mixed films with silica content of 20% or 50%, respectively, were prepared on slide glass substrate by spin-coating deposition. Hereafter, the titania–silica mixed films with 20% silica or 50% silica will be denoted as 80titania–20silica or 50titania–50silica, respectively. After spin-coating, the films were annealed in oxygen ambient at temperatures of 100–250 °C for 30–180 min. After these films were irradiated with UV-lamp (20 μW/cm$^2$), iterative measurements of contact angle using water droplets were carried out. The film thickness was measured by mechanical profilometry. The composition and crystalline structure of the spin-coated films were analyzed by X-ray photoelectron spectroscopy (Al $K_\alpha$ X-ray source) and X-ray diffraction (Cu $K_\alpha$ X-ray source), respectively.

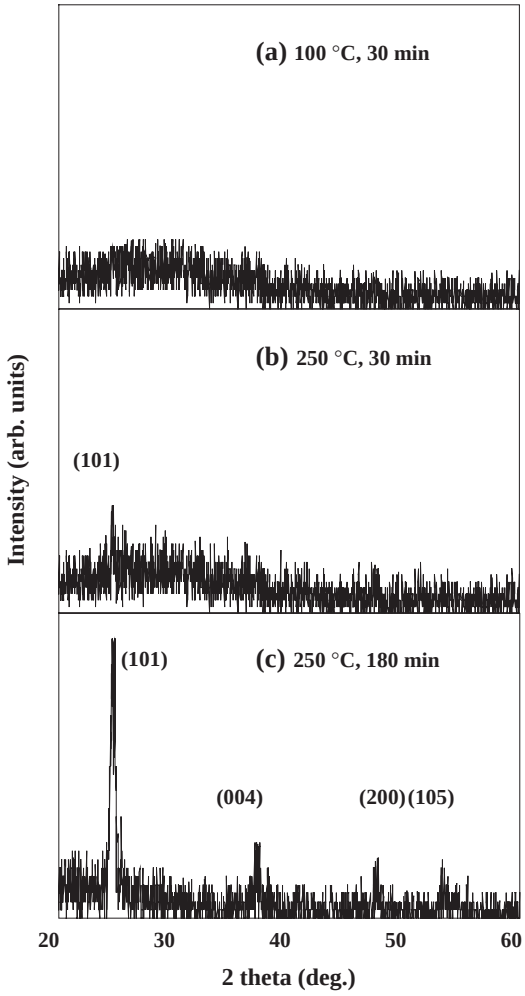


Fig. 2. Diffraction patterns of the titania films annealed (a) at 100 °C for 30 min, (b) at 250 °C for 30 min, and (c) at 250 °C for 180 min, respectively.

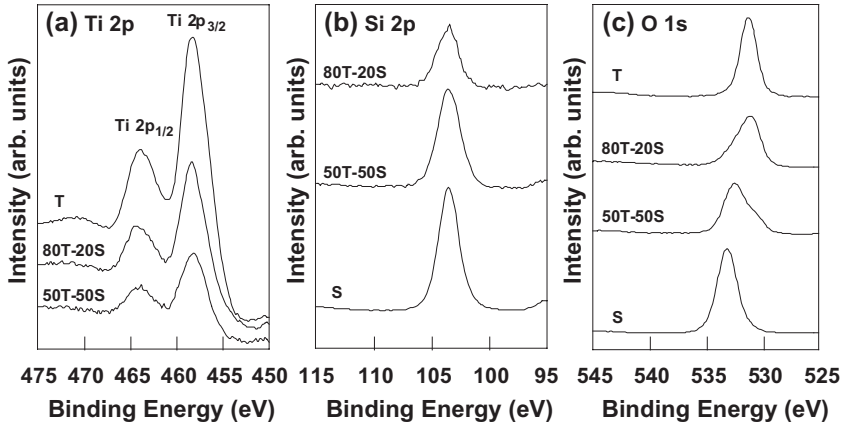


Fig. 1. XPS spectra for (a) Ti 2p, (b) Si 2p, and (c) O 1s, respectively. T, 80T–20S, 50T–50S, and S express titania, 80titania–20silica, 50titania–50silica, and silica, respectively. Spin-coated titania, 80titania–20silica, and 50titania–50silica films were annealed at 250 °C for 30 min.