Growth and surface treatment of TiO₂ nanorods using stearic acid solution

Sang-Hun Nam, Jin-Hyo Boo *

Department of Chemistry, Sungkyunkwan University, Suwon 440–746, South Korea

A R T I C L E   I N F O
Available online 11 June 2013

Keywords:
Hydrophobic
Stearic acid
Nanorod
TiO₂
Contact angle

A B S T R A C T
Titanium dioxide (TiO₂) nanorods were deposited on silicon substrates using titanium tetra-isopropoxide as a precursor via a metal-organic chemical vapor deposition method. TiO₂ nanorod film thickness was about 3.8 μm, and the observed contact angles of the TiO₂ surface were very low due to their super-hydrophilic properties. As a next step, TiO₂ nanorods were treated for 24 h with stearic acid molecules. Surface wettability changed from hydrophilic to hydrophobic by stearic acid treatment and the contact angle of TiO₂ nanorod film after treatment was approximately 119°.

1. Introduction

Super-hydrophobic properties can be found in nature in certain plant leaves. One example is the well-known lotus leaf [1], which has a water contact angle as great as 160° due to special surface nanostructures and wax functional groups [2]. These super-hydrophobic surfaces can be used in many industrial applications. Previous experiments have shown that appropriate deposition methods and functional group treatment by stearic acid [3,4] are needed for the fabrication of super-hydrophobic surfaces [5].

Here, TiO₂ nanorods were chosen as potential super-hydrophobic surfaces. This material is of interest due to its unique structure and properties [6,7]. After the initial observation of nanorods and the development of applications, there has been increased interest in such surfaces [8,9]. Nanorods have been synthesized for potential use in devices, as photo-catalysts and for other functional applications [10].

Synthesis of nanomaterials is typically by sol–gel, vapor phase transport, hydrothermal synthesis, arc discharge, electro-chemical synthesis or chemical vapor deposition [11]. There are many potential applications of TiO₂ nanorods, including use as a photocatalyst [10], gas and humidity sensors [12] and in solar cells [13]. In this study, the synthesis of TiO₂ nanorods by a metal-organic chemical vapor deposition (MOCVD) process is described.

Fatty acids are among the essential components of wax fabricated by plants [1,2]. With increasing chain length, they become insoluble in water and can form organized molecular film or even micelles on air–water interface due to essential components of wax fabrication. All these characteristics give them their wetting properties. Stearic acid, a C₁₈ fatty acid was chosen as a treatment material because it has a flexible saturated hydro-carbon chain that can stretch into a long zigzag shape. The focus of this study was to develop super-hydrophobic surfaces on TiO₂ nanorod arrays treated with stearic acid. We further extended this study by investigating the influence of the alkyl conformation chain of stearic acid that has high contact angle. Contact angle is often used to follow the self assembly of a mono-layer with long methyl-terminated alkane chains on oxide surfaces.

2. Experimental details

TiO₂ nanorods were deposited on silicon substrate using titanium isopropoxide (TTIP) as a precursor at 7 Pa by MOCVD using an indirect heating method. The heating temperature was kept at 500 °C as monitored by a k-type thermocouple. The precursor was kept at room temperature (25 °C). Also, N₂ gas was used as a bubbling gas for the organic-metal precursor with a flow rate of 20 sccm and O₂ gas was used as a reactive gas at flow rates of 5 or 15 sccm for the TiO₂ growth.

The stearic acid was prepared at a concentration of 0.05 M in ethanol. The TiO₂ nanorods were treated with a 50 mL stearic acid solution. They were then rinsed with water and ethanol, dried with N₂ gas, and then stored in a clean container.

Structural characterization of TiO₂ nanorods was performed using an X-ray diffractometer (XRD, RIGAKU, D/MAX-2200 Ultima) with CuKα radiation (λ = 0.15406 nm) in the Bragg–Brentano configuration. The angular range was 20 and 80°. The water contact angles of TiO₂ nanorod samples were evaluated by contact angle measurement. From the scanning electron microscopy (SEM, JEOL/JSM-6390A, 15.0 kV) investigation, surface and cross-sectional images were obtained. In order to identify the functional groups on stearic acid treated samples, Fourier-transform infrared (FT-IR) spectroscopy was performed in a wavelength from 600 to 3500 nm using transmission mode.

* Corresponding author. Tel.: + 82 31 290 7072.
E-mail addresses: askaeve@skku.edu (S.-H. Nam), jhboo@skku.edu (J.-H. Boo).
3. Results and discussion

Fig. 1 shows the cross-sectional images of TiO2 nanorods using 5 sccm (Sample A) and 15 sccm (Sample B) of O2 gas. Highly packed TiO2 nanorods were uniformly grown on the entire silicon substrate at 500 °C with different flow rates of O2 gas. Nevertheless, cross-sectional images for both samples are very similar. Also, the thicknesses of TiO2 nanorods were measured to be 3.72 μm at 5 sccm of O2 and 3.85 μm at 15 sccm of O2.

Fig. 2 shows typical crystal patterns with the TiO2 anatase phase at 500 °C with different O2 gas flow rates. This shows that the crystallinity of the TiO2 nanorods strongly depends on the O2 gas flow rate. TiO2 nanorods can be grown with low crystallinity at an O2 gas flow rate of 5 sccm. Atomic composition of the TiO2 nanorods strongly depended on the O2 gas flow rate. The most stoichiometric TiO2 nanorods were obtained at an O2 gas flow of 15 sccm. Growth direction is also affected by the O2 gas flow rate. However, when the O2 gas flow is greater than 25 sccm, anatase-type polycrystalline structures with various atomic compositions such as TiO2 and Ti3O4 were deposited [14].

Fig. 3 shows the vibration peaks of the stearic acid on the TiO2 nanorods surface. From the enhancement of peaks at $\nu_{as}(\text{COO}^-)$, $\nu_{s}(\text{COO}^-)$, $\nu_{as}(\text{CH}_3)$, and $\nu_{as}(\text{CH}_2)$ in TiO2 nanorods using O2 gas flow rates of 5 and 15 sccm, it can be inferred that stearate ions essentially coordinate to TiO2 with bidentate form [15]. However, low intensities for these peaks were found in the case of the 15-sccm O2 sample due to large differences in absorption number. In the case of 5-sccm O2 sample, the quantities of oxygen atoms in the thin film was reduced, creating oxygen vacancies because of the low flow rate of oxygen. Thus, absorption number of stearic acid decreased on the surface of the 5-sccm O2 sample [16].

We speculate that the organic molecules were chemically bonded to the surface of TiO2 films, and that the micro-structured surface was covered by a monolayer of stearic acid with the non-polar tails exposed to air. Fig. 4 shows the water contact angle on the stearic acid-treated surface. The nanorod surface changed from hydrophilic to hydrophobic after stearic acid treatment. Therefore, the differences in contact angle between the 5-sccm O2 sample and the 15-sccm O2 sample were due to the different absorption number of stearic acid resulting in the 15-sccm O2 sample a higher contact angle (119°) than the 5-sccm O2 sample (19°).

4. Conclusion

TiO2 nanorods with super-hydrophilic surface were deposited on a silicon substrate via MOCVD method. Then, we fabricated TiO2 nanorods with contact angle up to 119° using stearic acid treatment. Contact angles of TiO2 nanorods were controlled by varying the O2 gas flow rate. In the case of increased O2 gas flow, TiO2 nanorods showed strong absorption of non-polar tails on the surface, resulting in a higher contact angle value due to the hydrophobic nature of the non-polar tail. This denotes a specific influence due to the increase in oxide bonds of TiO2 and absorption number of stearic acid. We suggest that controlling the hydrophobicity or hydrophilicity of metal oxide nanorod surfaces can be applied in specific field.
Acknowledgments

This work was supported by grants from the Basic Science Research Program (S-2012-1120-000-1) and the Postdoctoral Research Program of Sungkyunkwan University (2013).

References


Fig. 4. Illustration of water contact angles between non-treated samples and stearic acid-treated samples.