

# Wettability Control of Photocatalytic Crystal Layers by Hydrophobic Coating and Subsequent UV Light Irradiation

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## Abstract

Wettability of solid surfaces with water is governed by surface morphology and composition. In this study, a surface finishing technique consisting of three processes, that is, nanotexturing by nanosized photocatalytic crystal coating, hydrophobic coating by chemical vapor deposition and subsequent ultraviolet light photolithography, was employed to form ultrahydrophobic/ultrahydrophilic solid surfaces. Flux grown nanosized  $K_4Nb_6O_{17}$  crystals were selected as a photocatalyst. A proper nanotexture of crystal layer surfaces enhanced their hydrophobicity. The rough solid surfaces modified by alkyl- and fluoro-alkyl silane were converted from ultrahydrophobic ( $>150^\circ$ ) to ultrahydrophilic ( $<10^\circ$ ) by photocatalytic oxidation using the  $K_4Nb_6O_{17}$  crystal layer. Fine pitch ultrahydrophobic/ultrahydrophilic patterns were readily obtained by photocatalytic lithography by use of area-selective 254 nm-ultraviolet light irradiation.

## 1. Introduction

Water- and oil-repellencies of solid surfaces have attracted much attention due to their potential application in various industrial fields. A wettability of solid surface with water is well-known to be governed by its chemical composition and nanotexture. Increasing a surface's water repellency can be achieved by both decreasing the free energy between it and water, and increasing its roughness [1,2]. Incorporating fluorine atoms, which have a small atomic radius and high electronegativity, can achieve a low surface free energy [3,4]. An ideally flat surface covered with regularly aligned and closely packed  $\text{CF}_3$  groups shows a water contact angle of about  $120^\circ$  [4]. To obtain a water-repellent surface showing a water contact angle greater than this value, a proper surface texture is crucial. The water-repellent leaves of lotus plants have inspired many artificial ultrahydrophobic surfaces. The secret of water-repellency of lotus leaves is the double roughness of their surfaces coupled with a waxy coating [5]. Indeed, surfaces with a water contact angle greater than  $150^\circ$  have been successfully fabricated so far by providing both a proper surface roughness and a low surface free energy [6-10]. We have previously reported on the fabrication of transparent ultra-water-repellent and patterned ultrahydrophobic/ultrahydrophilic polymeric substrates.

A variety of metal oxide compounds were studied for use as semiconductor photocatalysts, such as degradation of toxic substances, decomposition of pure water and photoactive electrodes for dye-sensitized solar cells [11-16]. Photoinduced decomposition of pure water on titanium oxide ( $\text{TiO}_2$ ) electrodes was first reported in 1972 [11]. After this discovery,  $\text{TiO}_2$

was widely studied, and has now become one of the most well-known semiconductor photocatalysts. Recently, besides  $\text{TiO}_2$ , semiconductor photocatalysts such as zinc oxide, titanates, niobates, and tantalates have been widely studied for achieving the conversion of photon energy into chemical energy [12-17]. Several types of niobate compounds, such as  $\text{KNbO}_3$ ,  $\text{KNb}_3\text{O}_8$ ,  $\text{K}_2\text{Nb}_8\text{O}_{21}$ ,  $\text{K}_3\text{NbO}_4$ ,  $\text{K}_4\text{Nb}_6\text{O}_{17}$ , and  $\text{K}_{5.75}\text{Nb}_{10.85}\text{O}_{30}$ , between  $\text{K}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  have been reported in recent years [12,14,16,17]. In our previous studies, various crystals of potassium niobates ( $\text{KNbO}_3$ ,  $\text{K}_2\text{Nb}_8\text{O}_{21}$ ,  $\text{K}_4\text{Nb}_6\text{O}_{17}$ , and  $\text{K}_{5.75}\text{Nb}_{10.85}\text{O}_{30}$ ) were grown from  $\text{K}_2\text{MoO}_4$ ,  $\text{K}_2\text{WO}_4$  and  $\text{KCl}$ . In particular,  $\text{K}_4\text{Nb}_6\text{O}_{17}$  is well-known as a typical photocatalyst under ultraviolet (UV) light irradiation.

In this paper, we demonstrate a surface-finishing technique to create ultrahydrophobic substrates and patterned ultrahydrophobic/ultrahydrophilic substrates. We have provided two crucial properties to silicon (Si) substrates. First, to form a proper surface texture on Si substrates, they were coated with nanosized photocatalytic  $\text{K}_4\text{Nb}_6\text{O}_{17}$  crystals. Subsequently, to reduce their surface free energy, a variety of hydrophobic layer coatings were formed on the nanotextured substrates by means of chemical vapor deposition (CVD). The water-repellency of the modified substrates is discussed in terms of their surface textures and chemical compositions. Furthermore, each of the ultra-water-repellent surfaces was photocatalytically micropatterned. Relatively low-energy UV light (wave length=254 nm) was selected as a light source because of much safer and cheaper than high-energy ones.

## 2. Experimental

Ultra-water-repellent and micropatterned ultrahydrophobic/ultrahydrophilic substrates were fabricated as schematically illustrated in Fig.1. First, nanotextured Si (100) wafers were prepared by means of squeegee technique. The photocatalytic crystal paste ( $\text{K}_4\text{Nb}_6\text{O}_{17}$ :Polyethylene glycol: $\text{H}_2\text{O}$  =7:3:10 in weight) was used to make the crystal layer having a rough surface. The used  $\text{K}_4\text{Nb}_6\text{O}_{17}$  crystals were transparent and colorless, and they were plate-like in form with well developed  $\{010\}$  faces. Their average size was about 100-300 nm. Detailed crystal growth procedures have been reported previously [16]. After the paste squeegee-coating, the substrates were heated at  $500^\circ\text{C}$  for 1.5 h. Subsequently, hydrophobic layers were prepared on the nanotextured surfaces by CVD using two types of organosilane precursors, that is, heptadecafluoro-1,1,2,2,-tetrahydrodecyl-1-trimethoxysilane [namely, fluoroalkylsilane, FAS,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ] and *n*-decyltrimethoxysilane [*n*-DS,  $\text{CH}_3(\text{CH}_2)_9\text{Si}(\text{OCH}_3)_3$ ]. For example, FAS molecule has the lower LUMO and HOMO so that these low energy levels lead to the lowest Fermi level (-0.20651 hartree). The nanotextured substrates were placed together with a glass cup filled with  $0.1 \text{ cm}^3$  organosilane liquid into a  $300 \text{ cm}^3$  Teflon container. The container was sealed with a cap and placed for 1 h in an oven maintained at  $150^\circ\text{C}$ . Consequently, the substrates became ultra-water-repellent. Next, each of ultra-water-repellent substrate samples was photocatalytically and photolithographically micropatterned. Through a line (200  $\mu\text{m}$ ) and space (100  $\mu\text{m}$ ) photomask placed on the sample surfaces, the samples were irradiated with UV light (about

1100  $\mu\text{W}/\text{cm}^2$ ) at a wavelength of 254 nm for 30 min under an air atmosphere.

The chemical compositions of the nanotextured, ultra-water-repellent and micropatterned surfaces were studied by means of Fourier-transform infrared spectroscopy (FTIR, JASCO, FT/IR-6100). Morphologies of the modified surfaces were observed by field emission scanning electron microscopy (FE-SEM, HITACHI, S-4100). Water contact angles of the modified Si substrate surfaces were measured using a contact angle meter (Kyowa Interface Science, DropMaster 500) based on the sessile water (distilled water) droplet measuring method, with a water drop of 2 mm in diameter. The measurements were conducted at around room temperature in air.

### 3. Results and Discussion

Fig.2 shows surface and cross-sectional FE-SEM images of the nanotextured Si wafer substrate coated with the nanosized photocatalytic crystals. The untreated Si substrate surface (Fig.2a) was completely flat, while the crystal-coated substrate surface (Fig.2b) appeared to be rough. As seen in Fig.2c, the crystal layer had a porous structure, and its thickness was approximately 17  $\mu\text{m}$ . Each water contact angle of the Si surfaces before and after the crystal coating was less than  $5^\circ$ .

Hydrophobic layers were formed on the nanotextured substrate surfaces by means of CVD. Fig.3 shows FTIR spectra obtained from the nanotextured substrate with or without the hydrophobic layers (Fig.3a: FAS-17 and Fig.3b: *n*-DS). Absorption bands due to carbon,

hydrogen and fluorine appeared at 1260-1230  $\text{cm}^{-1}$  ( $\text{CF}_3$  stretching), 1220-1200  $\text{cm}^{-1}$  ( $\text{CF}_2$  asymmetric stretching), 1160-1140  $\text{cm}^{-1}$  ( $\text{CF}_2$  symmetric stretching), 1130-1100  $\text{cm}^{-1}$  ( $\text{CF}_2$  symmetric stretching) and 1090-1060  $\text{cm}^{-1}$  (Si-O-Si stretching) (Fig.3a) and 2970-2950  $\text{cm}^{-1}$  ( $\text{CH}_3$  asymmetric stretching), 2940-2900  $\text{cm}^{-1}$  ( $\text{CH}_2$  asymmetric stretching) and 2870-2840  $\text{cm}^{-1}$  ( $\text{CH}_2$  symmetric stretching) (Fig.3b). Thus, it was confirmed that hydrophobic functional groups had been introduced onto the nanotextured surfaces.

Figure 4 shows photographs of a water droplet on the Si substrate treated with the two-step process. As clearly shown in Fig.4, the FAS-coated (Fig.4a) and the *n*-DS coated (Fig.4b) surfaces gave the required high contact angle (above  $150^\circ$ ) between the water and the surfaces, and so result in less wettable surfaces. Subsequently, the ultra-water-repellent surface with the photocatalytic crystal and FAS layers was photocatalytically modified. Photocatalytic  $\text{K}_4\text{Nb}_6\text{O}_{17}$  crystals can act as a sensitizer for light-reduced redox processes due to its electronic structure. When UV light ( $< 365 \text{ nm}$ ) was irradiated to the crystal layer, an electron is promoted from the valence band into the conduction band, leaving a hole behind. The electrons and holes react with electron donors and acceptors adsorbed on the crystal surfaces or within the surrounding electrical double layer of the charged surfaces. The holes are strong oxidants and the electrons are good reductants [18]. In our study, oxygen will be present to act as the primary electron acceptor. Therefore, photodegradation reactions of hydrophobic functional groups will utilize the oxidizing power of the holes and various activated oxygen species. Before the UV light (254 nm) irradiation, the FAS-nanotextured

surfaces showed ultra-water-repellency with a water contact angle greater than  $150^\circ$ . As clearly shown in Fig.5, the water contact angle values drastically decreased with increasing UV light irradiation times, and they reached less than  $5^\circ$  (20 min). On the other hand, the water contact angle of the FAS-coated Si surface without the photocatalytic layer was almost constant during UV light irradiation. When the UV light was irradiated onto the ultra-water-repellent surface having a proper nanotexture and a hydrophobic layer, surface terminating hydrophobic functional groups changed chemically to hydrophilic functional groups (e.g., hydroxyl groups).

The ultra-water-repellent surface was photocatalytically and photolithographically micropatterned. Fig.6 shows optical micrograph of the UV light-micropatterned surface. In this figure, the colored and white lines, respectively, correspond to ultrahydrophilic and ultrahydrophobic regions. Since the difference in the water contact angle between hydrophobic and hydrophilic areas is greater than  $150^\circ$ , each water colored by methylene blue was absorbed only into the hydrophilic regions (porous photocatalytic crystal layer) without making contact with adjacent water drops.

#### 4. Conclusions

We have succeeded in fabricating ultra-water-repellent substrates and ultrahydrophobic/ultrahydrophilic substrates by a multistep process, that is, nanosized photocatalytic crystal layer, CVD and UV light photolithography. Control of the surface

nanotexture and functional groups is crucial in order to attain ultra-water-repellency. Since the nanotexture formed by the photocatalytic nanosized  $K_4Nb_6O_{17}$  crystals remained completely after the hydrophobic layer coating, the surface-modified solid surfaces showed ultra-water-repellency with a water contact angle greater than  $150^\circ$ . When UV light was sectionally irradiated onto ultra-water-repellent surfaces, C, F and H atoms in the FAS and *n*-DS layers were area-selectively converted to volatile species, and were finally removed. Consequently, the surfaces became hydrophilic so as to show a water contact angle of less than  $10^\circ$ , and well-defined ultrahydrophobic/ultrahydrophilic micropatterns were fabricated on the solid surfaces.

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## Figure captions

- Figure 1 Schematic diagram of the ultra-water-repellent and the micropatterned ultrahydrophobic/ultrahydrophilic substrate preparation process by a multistep process.
- Figure 2 Surface and cross-sectional SEM images of the nanotextured Si substrate coated with the nanosized photocatalytic crystals. (a) Surface image of untreated Si wafer, (b) surface image of the crystal layer and (c) cross-sectional image of the crystal layer.
- Figure 3 FTIR spectra of the photocatalytic  $K_4Nb_6O_{17}$  crystal layer surfaces with or without (a) FAS- and (b) *n*-DS-hydrophobic layers.
- Figure 4 Photographs of a water droplet on the Si substrate treated with the two-step process. (a) FAS- and (b) *n*-DS-coated surface.
- Figure 5 Variation in the water contact angle with UV light irradiation time.
- Figure 6 Optical micrograph of the UV light-micropatterned surface.

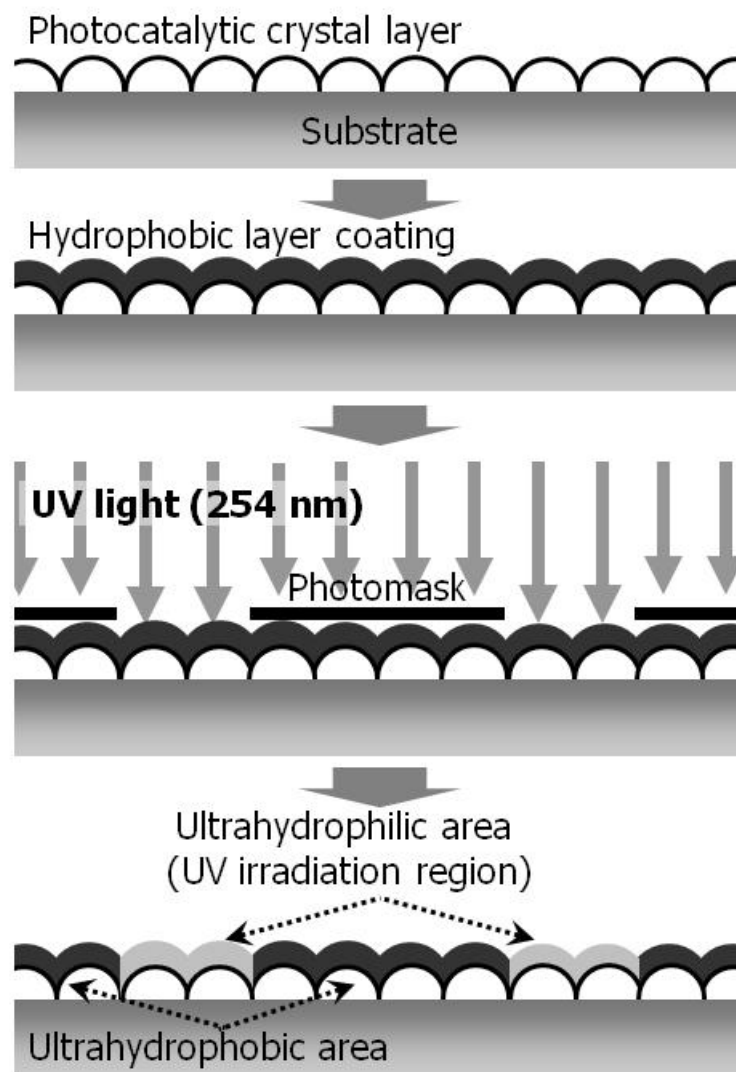


Figure 1 Teshima et al.

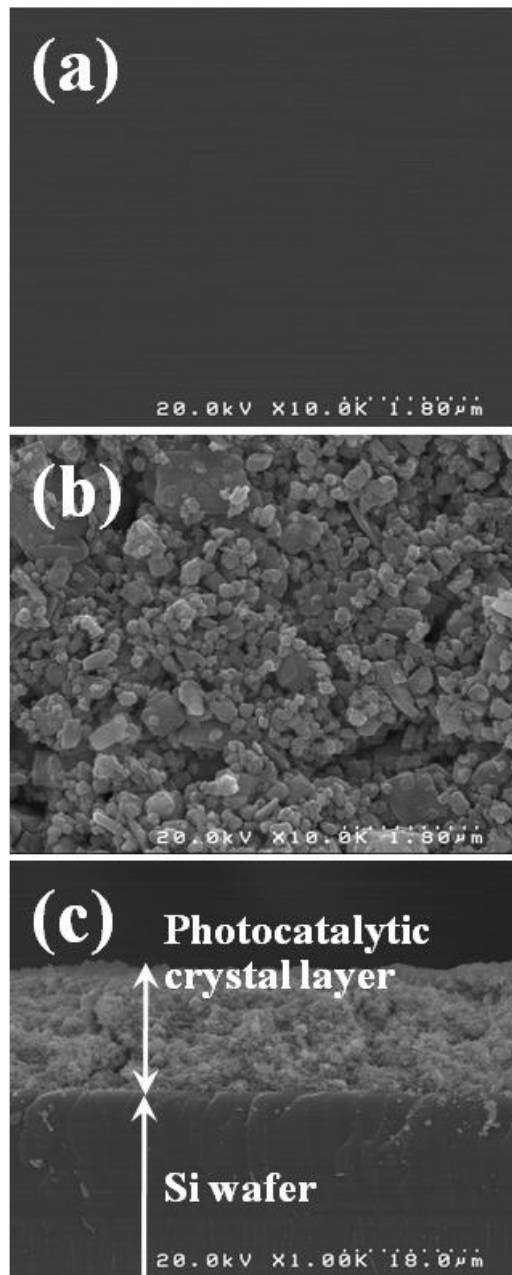


Figure 2 Teshima et al.

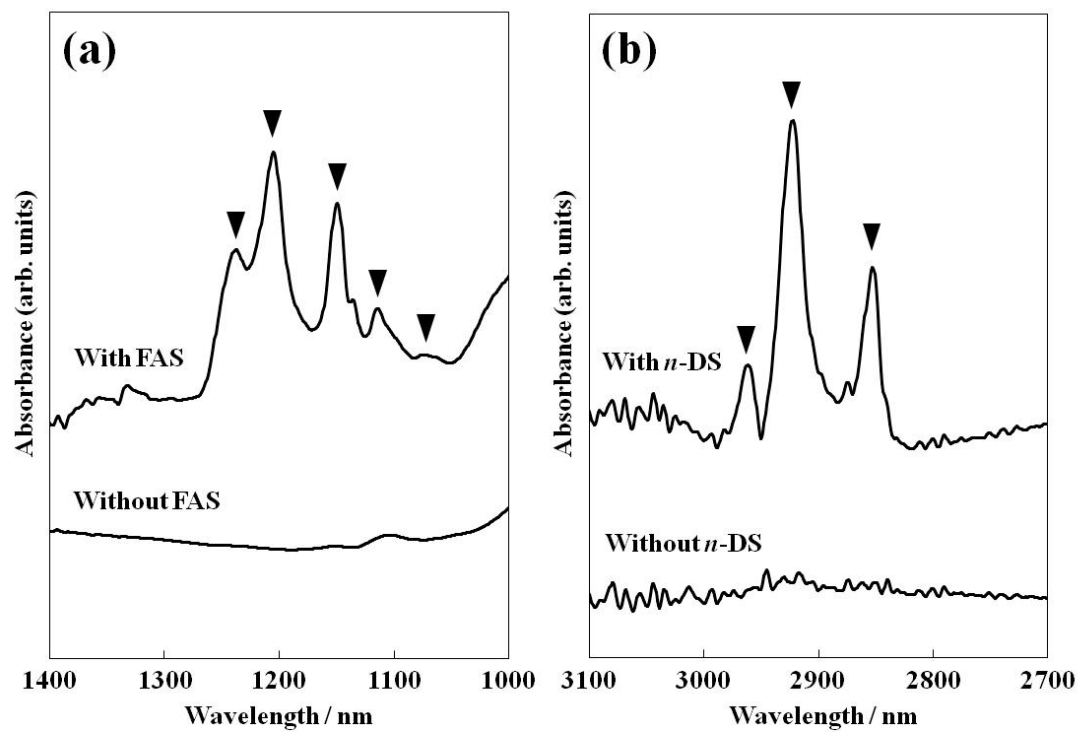


Figure 3 Teshima et al.

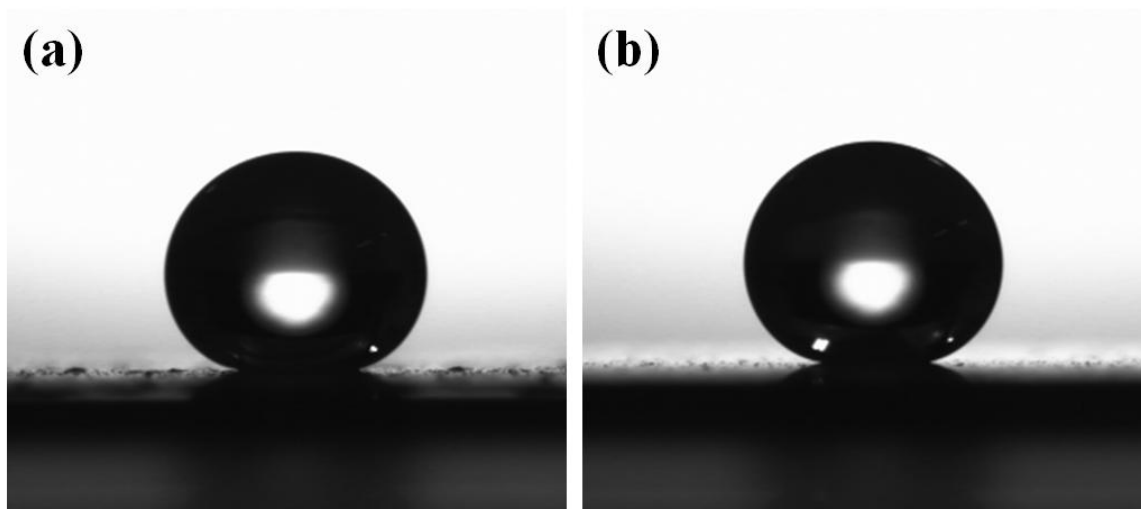


Figure 4 Teshima et al.

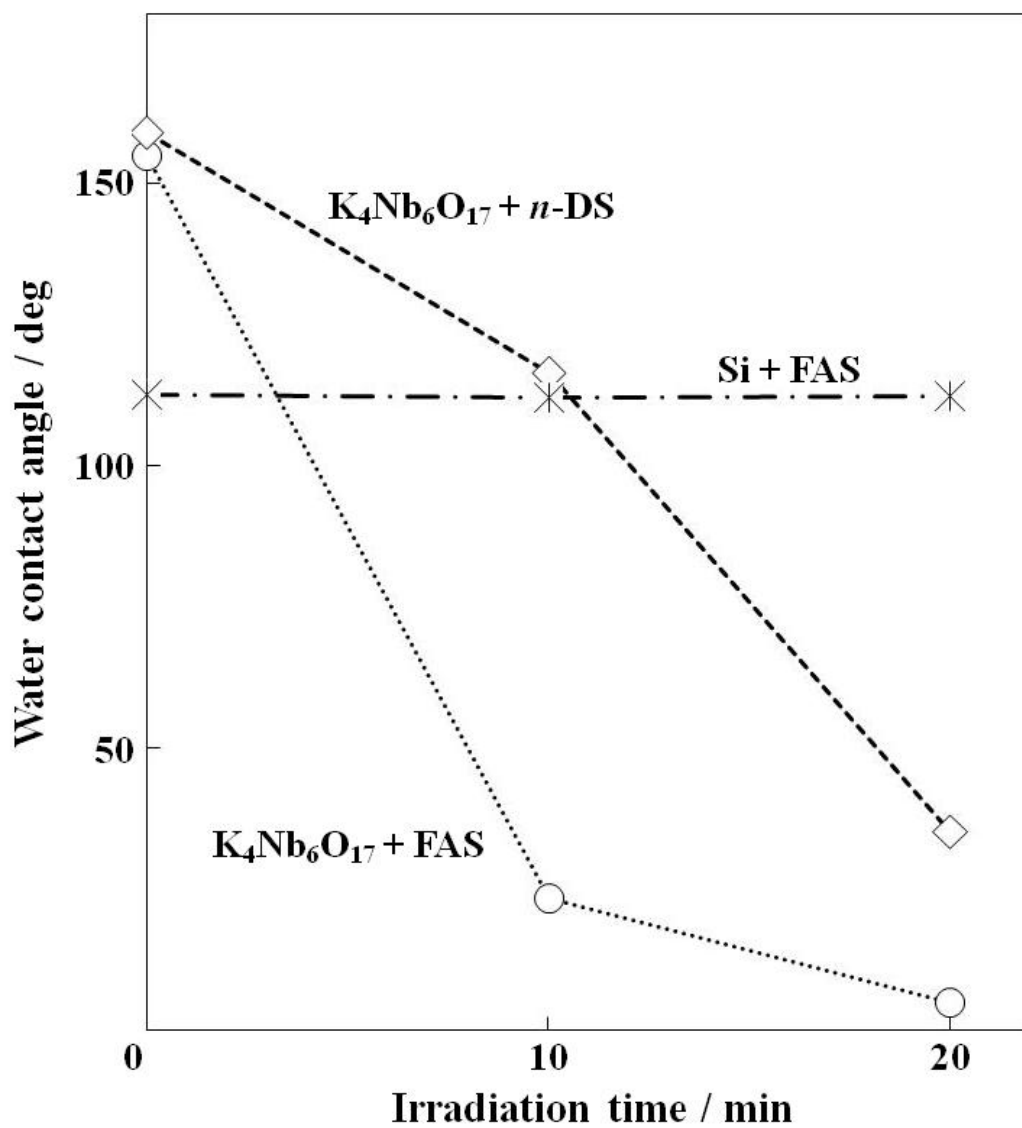


Figure 5 Teshima et al.



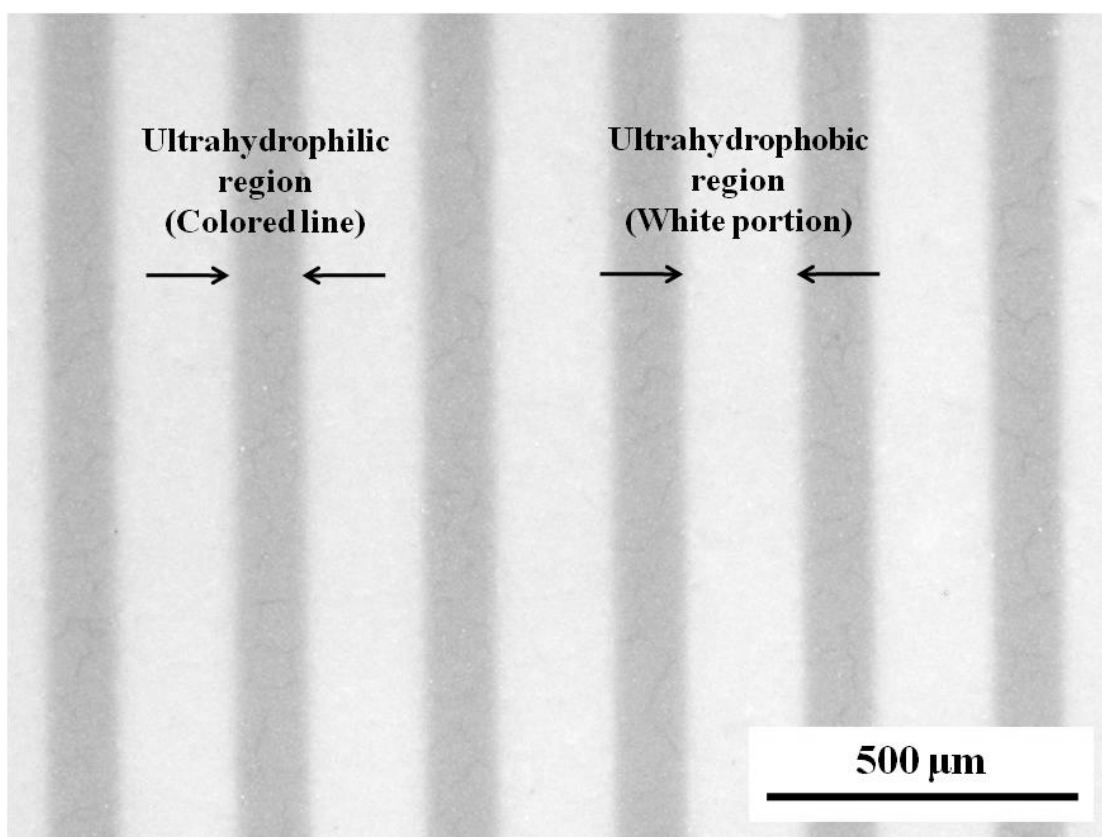


Figure 6 Teshima et al.