The Novel Wetting Behavior of Periodic Ti<sub>x</sub>Sn<sub>1−x</sub>O<sub>2</sub> Nanostructures

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Regular arrays of Ti<sub>x</sub>Sn<sub>1−x</sub>O<sub>2</sub> nanostructures were produced through glancing angle sputter deposition onto self-assembled close-packed arrays of 200-nm-diameter and 1-µm-diameter polystyrene microspheres respectively. The anisotropic nanoflakes grown on 200-nm-diameter polystyrene microspheres exhibited macroscopic-wetting anisotropy, with the apparent contact angle observed parallel to the direction of the nanoflakes larger than the apparent contact angle in the perpendicular direction. This anisotropic wettability is ascribed to the difference of the three-phase contact line structure for the parallel and perpendicular direction, resulting from the anisotropic topography. Compared with the nanoflakes, the “spheric shells” were obtained using the 1-µm-diameter polystyrene microsphere templates, on which the apparent contact angle of the drop was nearly uniform along the contact line. After annealing at 823 K for 3 h, both the films were crystallized to TiO<sub>2</sub>/SnO<sub>2</sub> composite and maintained good thermal stability in the morphology. It was shown that the “spheric shells” can be reversibly switched between hydrophobicity and superhydrophilicity by alternating visible light illumination and dark storage. This novel visible light-responsive behavior was explained by the enhanced separation efficiency of photogenerated electron–hole pairs in the TiO<sub>2</sub>/SnO<sub>2</sub> composite.

Keywords: Ti<sub>x</sub>Sn<sub>1−x</sub>O<sub>2</sub> nanostructures, glancing angle sputter deposition, anisotropic wetting, visible light-induced wettability transition

1. Introduction

Control over the wettability of surfaces as well as the preparation of functional surfaces with special wetting properties has stimulated intense research efforts due to their importance in both fundamental studies and practical applications. In the past years there has been an increasing interest in manipulating the wettability of solids by tuning the surface geometry and chemistry. For example, inspired by the rice leave surfaces, the anisotropic wetting surfaces which are fabricated through chemical patterning or surface topography, have attracted remarkable attention owing to their great potential in microfluidic devices, evaporation-driven formation of patterns, and self-cleaning coatings. Likewise, stimuli-responsive smart materials that can be reversibly switched between hydrophobicity and hydrophilicity under the action of external stimuli have generated great interest due to a wide range of potential applications. Among these stimuli-responsive functional materials, some semiconductor oxides, such as TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, and SnO<sub>2</sub>, exhibit pronounced wettability transition between hydrophobicity and hydrophilicity upon ultraviolet (UV) irradiation by combining the surface roughness with a change of surface chemistry. They have been widely studied because of the clear advantages over other organic molecules in terms of structural and chemical stability, low toxicity, and remarkably larger wettability changes.

However, many questions are still in debate and need to be clarified, especially about the mechanism of these special wetting properties. Wenzel and Cassie formulas have been widely used to explain the wetting behaviors of surfaces over the past years. However, they often fail to correctly predict contact angles on heterogeneous surfaces. It was suggested that the contact angle is a function of contact line structure, and that the kinetics of droplet movement, rather than thermodynamics, control wetting of heterogeneous surfaces. Therefore, the two prevailing theories are insufficient to understand the anisotropy in the wetting. Herein, we report periodic arrays of Ti<sub>x</sub>Sn<sub>1−x</sub>O<sub>2</sub> nanostructures fabricated by glancing angle sputter deposition, and the films prepared on 200-nm-diameter and 1-µm-diameter polystyrene microsphere templates showed sharply different wetting behavior due to the surface morphology. The anisotropic wettability was observed on the anisotropic nanoflakes using 200-nm-diameter polystyrene microsphere templates. As often mentioned in the literature, the anisotropic wettability can be induced by anisotropic topography composed of micron-scale grooves, however, whether the sub-micron nanostructures can lead to anisotropic wettability is seldom studied. This finding helps the understanding of the effect of the three-phase contact line structure on the wetting of surfaces, which can inspire us to design the surfaces with respect to shape and extent of the three-phase line, instead of decreasing the solid-water contact area only.

Besides, the stimuli-responsive wettability change of post-annulled films was studied. It was found that the film grown on 1-µm-diameter polystyrene spheres showed superhydrophilicity upon visible light irradiation and exhibited a reversible conversion between hydrophobicity and superhydrophilicity by alternating visible light illumination and dark storage. Although there have been many reports on the light-responsive smart materials, they are mostly focused on the UV irradiation, while the visible light-induced wettability transition is rarely reported. The realization of extending light-response to visible light range arises from the improved separation of photogenerated electron–hole pairs due to the potential energy differences between SnO<sub>2</sub> and TiO<sub>2</sub>, and will be useful to engineer visible light-manipulated, oxide-based functional surfaces for intelligent microfluidic devices, microreactors, or self-cleaning coatings.

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2. Experimental Details

The Ti₃Sn₁₋ₓO₂ nanostructures were prepared in an ultrahigh vacuum magnetron sputter deposition system on Si(001) substrates that were patterned with 200-nm-diameter and 1-µm-diameter hexagonal close-packed polystyrene microspheres respectively. Ti₃Sn₁₋ₓO₂ depositions were carried out using a 60-mm-diameter Ti target (99.999% in purity) and a 60-mm-diameter SnO₂ target (99.9% in purity) mounted at an angle of 120° with respect to each other, and with the Ti target back to the substrate. The deposition angle α (the angle between the trajectory of the incident vapor flux and the substrate normal), which was controlled by the substrate position with respect to the Ti target, was selected to be 85°. Sputtering was carried out at 0.15 Pa which was held constant during all depositions in 99.999% pure Ar. Power-regulated DC and RF power supplies were used to provide the discharge current of 0.25 A at 340 V for Ti, and a radio frequency current of 130 mA at 500 V for SnO₂. The Ti₃Sn₁₋ₓO₂ nanostructures were yielded with the simultaneous deposition from the sputtering sources of Ti and SnO₂ onto a stationary substrate. The morphology of all samples was examined by a scanning electron microscope (SEM), with their structure identified by X-ray diffraction (XRD) analysis, and the contact angle was measured using the sessile drop method.

3. Results and Discussion

The morphology of the Ti₃Sn₁₋ₓO₂ nanostructures grown on 200-nm-diameter and 1-µm-diameter polystyrene microspheres is shown in Figs. 1(a) and 1(b) respectively. Arrays of well-separated Ti₃Sn₁₋ₓO₂ nanostructures were produced. The regular hexagonal arrays replicate the close-packed structure of the polystyrene microspheres, as shown in Fig. 1(a). The formation of nanoflakes can be explained by the mechanism of GLAD. As GLAD is a physical vapor deposition process in which the incident flux impinges the substrate from an oblique angle, causing atomic shadowing and the resulting highly porous nanostructures,8-11 the morphology of nanostructures is closely related to the direction of the incident flux. With the incident flux from lateral SnO₂ target, the direction of the growth front is changed from straight up to lateral growth, leading to an increase of the growth rate in the direction parallel to the SnO₂ flux and a decrease in the perpendicular direction.12 As a result, the nanostructures are deformed by the anisotropic lateral growth and present the anisotropic morphology of melon seed-shaped nanoflakes. With the size of polystyrene microsphere templates increased to 1 µm, the nanostructures evolve into isotropic “spheric shells” covering the polystyrene microspheres, as shown in Fig. 1(b). It’s consistent with the growing mechanism of nanostructures. For the deposition layer is relatively thin, the anisotropic lateral growth is overwhelmed by the effect of templates gradually with the increase of the template size, causing the degeneration from nanoflakes to isotropic “spheric shells”.

The contact angle measurement indicates that the apparent contact angle observed in the direction parallel to the nanoflakes is larger than that in the perpendicular direction, as shown in Figs. 2(b) and 2(c) [the measurement directions for nanoflakes are marked in Fig. 2(a)]. This anisotropic wetting behavior can’t be explained just by Wenzel and Cassie formulas. Because Wenzel’s and Cassie’s equations are valid only to the extent that the structure of the contact area reflects the ground state energies of contact lines and the transition states between them,7,8 while on anisotropic topography surfaces the wettability is determined by the activation energies that must be overcome in order for contact lines to move from one metastable state to another. The drop gets trapped in the observed state which is a local low energy state well separated from the “neighboring” lower energy states by an energy barrier but not necessarily the lowest energy state.13 Therefore, it’s the interactions at the contact line that govern the wetting of surfaces, rather than the contact area. A continuous short three-phase contact line is preferable for the spreading out of droplets; however, discontinuous three-phase contact line will cause the energy barrier for the movement of the three-phase line and introduce strong resistance against the stretching of drops.14 For the anisotropic nanoflakes, larger energy barrier is generated in the movement direction perpendicular to the nanoflakes, which leads to the squeezing and pinning of the drop in the parallel view, and thus the anisotropic wettability.

![Fig. 1 Scanning electron microscopic images of Ti₃Sn₁₋ₓO₂ films deposited on 200 nm (a) and 1 µm (b) polystyrene microspheres.](image_url)
The wettability of “spheric shells” was also measured and presented isotropic wetting with contact angles of 119.0° and 121.3° from two directions. This result confirms that the sub-micron-scale geometry anisotropy can generate macroscopic anisotropic wettability, which is valuable to uncover the mechanism of anisotropic wetting behaviors.

The structures of as deposited films were identified by X-ray diffraction (XRD), indicating the amorphous state in both the films. It demonstrated that the appropriate annealing temperature for the Ti<sub>x</sub>Sn<sub>1-x</sub>O<sub>2</sub> films was 823 K, with crystallization of the structure and thermal stability in the morphology. Figure 3 shows the XRD result of the as deposited film and the films annealed in a tube furnace at 823 K for 3 h. The post-annealed films using 200-nm and 1-µm polystyrene spheres are marked as 1# and 2# respectively. It indicates that film 1# is composed mainly of rutile SnO<sub>2</sub>, along with cubic SnO<sub>2</sub> (CaF<sub>2</sub> structure), anatase and rutile TiO<sub>2</sub>. And the film 2# consists of rutile SnO<sub>2</sub> and TiO<sub>2</sub>. Besides, the energy-dispersive X-ray spectrum (EDS) result shows that the contents of Ti for film 1# and 2# are 30.74% and 30.67% respectively.

The wettability of the post-annealed films was evaluated by contact angle measurements. Surprisingly, the film prepared on 1-µm-diameter polystyrene microspheres showed superhydrophilicity when exposed to visible light. The spherical water droplet spreads out on the surface immediately with a CA of about 8.9°, as shown in Fig. 4(a). The film was stored in the dark for two weeks subsequently, and demonstrated the surface wettability conversion from superhydrophilic to hydrophobic with an increase in the CA up to ~109.5° [Fig. 4(b)]. The process can be carried out over several cycles, and good reversibility of the surface wettability was observed [Fig. 4(c)]. It proves that by visible light illumination and dark storage the superhydrophilicity and hydrophobicity on the film can be reversibly switched.

Although the related mechanism is still controversial, this conversion is generally believed to be initiated by photo-generated holes that react with lattice oxygen to form surface oxygen vacancies. These defects are then able to promote dissociative adsorption of atmospheric water, which ultimately leads to an increase in surface hydroxylation. The increase of surface hydroxylation would promote adhesion of ordered H<sub>2</sub>O multilayers, resulting in the improvement of the surface hydrophilicity. Upon prolonged storage in the dark, ambient oxygen gradually removes the newly implanted hydroxyl groups from the semiconductor surfaces, because oxygen adsorption is thermodynamically more
stable. The surface thus evolves back to its original state (before any illumination), and the hydrophobic character is re-established.

As discussed above, the photogenerated hole that creates oxygen vacancies at the semiconductor surface to which water molecules kinetically coordinate is the predominant factor for the light-responsive wetting change. However, the fast recombination rate of the photogenerated electron–hole pairs hinders the proceeding of this process. The novel visible light-induced wettability transition we obtained can be attributed to the increase in the efficiency of interfacial charge separation by combining the two semiconductors with different energy levels. The energy levels of the valence and conduction bands are 2.7 and $-0.5$ V for TiO$_2$, and 3.7 and 0.0 V (vs. NHE at pH 7) for SnO$_2$. Upon photoexcitation of TiO$_2$/SnO$_2$ composite, photogenerated-electrons on TiO$_2$ flow into the conduction band of SnO$_2$, while holes diffuse toward the TiO$_2$ surface. Hence, the reaction efficiency is promoted due to the electron transfer from TiO$_2$ to SnO$_2$, explaining the visible light-responsive wetting transition. However, for the post-annealed film on 200-nm polystyrene microspheres, the contact angle can reach just 65.9° and 78.0° (for two directions) after exposure to visible light. The desired superhydrophilicity state isn’t achieved, probably owing to the energy barrier for the moving of three-phase contact lines brought by the morphology of nanoflakes. Although there are still questions to be further studied, this result provides an approach to achieve visible light-manipulated wettability by combining two photosensitive semiconductors, and the semiconductor composite with controllable composition is promising for a wide range of applications.

It must be noted that the Ti$_x$Sn$_{1-x}$O$_2$ films possess excellent antireflection effects by creating a gradient of refractive index, which has been reported in our previous work. As known, antireflection and special wettability are often competitive properties, since the rough surface morphology that is necessary to induce special wettability often leads to severe light scattering. This problem greatly restricts the practical applications. Therefore, the realization of special wettability on antireflective films is of great significance and can be employed to develop coatings for various substrates with simultaneous antireflective, self-cleaning and antifogging behavior.

### 4. Conclusions

The manipulation of surface wettability is important for many biochemical processes and industrial applications. As surface wettability is mainly dependent on surface geometry and chemistry, control over surface topography and chemical composition of films are two approaches to tailor wettability and thus develop functional surfaces. Herein arrays of Ti$_x$Sn$_{1-x}$O$_2$ nanostructures have been prepared on different-sized polystyrene microsphere templates by glancing angle sputter deposition, leading to different surface morphology. The anisotropic nanoflakes and isotropic “spheric shells” obtained on 200-nm-diameter and 1-µm-diameter polystyrene microspheres respectively were found to exhibit remarkable contrast in wettability, ascribed to the energy barrier for the moving of three-phase contact lines which is determined by the surface topography. On the other hand, the post-annealed film using 1-µm-diameter polystyrene microsphere templates can be reversibly switched between hydrophobicity and superhydrophilicity by alternation of visible light illumination and dark storage. The wettability transition is induced by a progressive increase in the degree of surface hydroxylation upon the photoexcitation, which is closely related to the surface chemical composition. The enhanced separation of photogenerated electron–hole pairs in the TiO$_2$/SnO$_2$ composite is considered to be responsible for this visible light-responsive wettability change. In summary, some novel wetting behaviors were observed in the periodic Ti$_x$Sn$_{1-x}$O$_2$ nanostructures by tailoring the surface morphology and chemical composition, which opens up the prospect of designing special wetting surfaces combined with antireflection properties and further exploring the mechanisms of the special wettability.

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### REFERENCES