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Design and fabrication of a nanostructured surface combining antireflective and enhanced-hydrophobic effects

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Abstract
Herein, we propose a special type of periodic subwavelength structure, which is optically an effective gradient-index (GRIN) antireflective surface that also exhibits enhanced-hydrophobic behaviour. Our new concept was developed adopting both the effective medium theory (EMT) and Wenzel's wettability model. To demonstrate the concept, an inverted pyramid structure was fabricated by electron beam (EB) lithography and anisotropic etching. The experimental data was found to be in good agreement with the theoretical prediction. Some potential applications that can benefit from this combination of antireflection and enhanced-hydrophobicity features are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Both antireflective and super-hydrophobic effects can be observed on surfaces with small structures. For example, the eyes of some species of moths can be considered a type of antireflective structure. This type of periodic structure, about 200 nm in size and which appears as a grainy protuberance, prevents reflected light from giving away the moth's location to its enemies (Bernhard 1967). The optical properties of various types of periodic subwavelength structures have been studied, which include not only antireflective surfaces but also polarizers, polarized beamsplitters (Glaser *et al* 2002), waveplates (Cescato *et al* 1990), binary Fresnel lenses (Mait *et al* 1998) and binary blazed gratings (Lalanne and Morris 1997). On the other hand, super-hydrophobic surfaces, whose contact angles are larger than 140°, have attracted attention because of their self-cleaning effect (Barthlott and Neinhuis 1997). Such a feature can be observed on lotus leaves as well as in many other kinds of leaves in nature. This feature allows the leaves to repel rain as well as keep contamination away so that the purity of the leaves is maintained. In recent years, super-hydrophobic surfaces have been produced artificially. Previous research has identified surface structures as the origin of the super-hydrophobicity and has demonstrated that the fabrication of super-hydrophobic structured surfaces is possible (Shibuichi *et al* 1996, Bico *et al* 1999).

In this paper, our research on combining antireflective and super-hydrophobic effects on structured surfaces is reported (Xu *et al* 2003, Artus *et al* 2006, Prevo *et al* 2007). The main motivation behind the integration of these two features lies in the fact that various important applications require having both effects. For example, car windshields and building glass can benefit from the self-cleaning effect associated with super-hydrophobic surfaces. However, transparency is a prerequisite in these applications. Since super-hydrophobic surfaces often suffer from strong scattering or diffraction effects due to its rough structured surfaces, only limited implementation was attempted in the past. However, we can overcome this dilemma by combining both antireflective and super-hydrophobic effects. Moreover, surfaces with both effects can be useful for optical devices which operate under harsh outdoor environments such as solar cells, display panels or light-emitting diode (LED) lamps. By building a self-cleaning feature into a product and not having it degrade transmission, such devices can keep contamination to a minimum so that long-term optical performance can be maintained.

At first glance, combining both antireflection and enhanced-hydrophobicity features seems impractical and not feasible. In fact, since typical super-hydrophobic surfaces are very rough, previous discussions have indicated a trade-off between the scattering and the hydrophobicity (Duparre *et al* 2002, Prevo *et al* 2007). Duparre *et al* (2002) quantitatively analysed the scatter loss and hydrophobicity of a rough surface and implied there was a trade-off in having both features in the same structure. One way to overcome this trade-off dilemma is to make a random structure with the length scale much smaller than the wavelength to minimize scattering. For example, Xu *et al* (2003) produced a porous silica film using a sol–gel process while Artus *et al* (2006) obtained a silicone nanofilament using chemical vapour deposition. Both produced structured materials which were effective homogeneous films optically, yet rough enough to exhibit super-hydrophobicity. In this paper, we propose another approach in which a periodic subwavelength structure is used. This special type of structure is designed as an effective gradient-index (GRIN) antireflective surface for light and, simultaneously, as a super-hydrophobic surface for water. Compared with the random structure previously proposed, the performance of our periodic subwavelength structure is predictable and the design feasible, as demonstrated by our theoretical prediction agreeing well with the experimental results. Our structure also possesses a better broad band performance in antireflection since the gradient-index concept is used instead of a wavelength-dependent thin-film interference. Moreover, the concept of form birefringence can also be applied to periodic subwavelength structures to produce polarization-dependent characteristics (Cescato *et al* 1990).

2. Theory

To produce the antireflective effect, we considered the design of periodic subwavelength structures. The optical properties of the periodic subwavelength structure can be easily estimated by the effective medium theory (EMT) (Lalanne and Hutley 2003, Yeh 1991), which provides insight into how to design a proper structure. Under certain constraints (Lalanne and Hutley 2003) we can use the EMT method to obtain the approximate correct optical properties if the structure is ignored and each layer is treated as an equivalent homogeneous medium whose refractive index is determined by the filling factor of the structure. For a two-dimensional rectangular grating, the EMT gives the upper bound and lower bound for the value of the effective index $\varepsilon_{\mathrm{eff}}$ (Jackson 1999, Chen and Craighead 1995)

$$\frac{1}{\varepsilon_{\mathrm{upp}}} = \frac{(1-f_x)}{\varepsilon_1} + \frac{f_x}{f_y\varepsilon_2 + (1-f_y)\varepsilon_1} \quad (1)$$

$$\varepsilon_{\mathrm{low}} = (1-f_y)\varepsilon_1 + f_y[f_x/\varepsilon_2 + (1-f_x)/\varepsilon_1]^{-1}, \quad (2)$$

where f_x and f_y are the filling factors of the structure along the x and y directions; ε_1 and ε_2 are the permittivities of the air and substrate; and where the effective index $\varepsilon_{\mathrm{eff}}$ lies between $\varepsilon_{\mathrm{upp}}$ and $\varepsilon_{\mathrm{low}}$.

With EMT, it is possible to design a surface profile whose optical properties are similar to a GRIN antireflective surface (Enger and Case 1983, Ono *et al* 1987, Raguin and Morris 1993, Kanamori *et al* 1999), whose effective refractive index changes slowly with depth from the index of air to that of the substrate. The reflection is reduced when there is no abrupt change of the refractive index. The GRIN antireflective surface has the advantage of a broadband performance over the thin-film antireflective coating since the reflection reduction is not attributed to the wavelength-sensitive destructive interference. To analyse the structure completely and correctly, the EMT estimation can be followed by applying rigorous methods such as rigorous coupled-wave approach (RCWA) (Moharam and Gaylord 1982) and finite element method (FEM).

Typically, Wenzel's model and Cassie's model are the two models most often adopted to explain the super-hydrophobic mechanism (Wenzel 1936, Cassie and Baxter 1944, Nakajima *et al* 2001, Quere 2002, Blossey 2003). These models, as shown in (3) and (4), take the surface structure into account by modifying Young's equation, which determines the contact angle on smooth surfaces:

$$\cos\theta_{\mathrm{W}} = r\cos\theta_{\mathrm{Y}}, \quad (3)$$

$$\cos\theta_{\mathrm{C}} = f\cos\theta_{\mathrm{Y}} + (1-f)(-1). \quad (4)$$

In the models shown above, r is the ratio between the actual surface area and the projected surface area and it equals one for a smooth surface and has a value greater than one for a rough surface; θ_{W} and θ_{C}, respectively, denote the contact angle predicted by Wenzel's and Cassie's models, with f denoting the filling factor of the structure.

For a structured surface, Wenzel's model assumes that a liquid intrudes into the structure and fills up the grooves. Thus this model implies that smooth hydrophobic surfaces become more hydrophobic if the structure is imparted. Cassie's model, on the other hand, considers that air is trapped inside the grooves. For a simple binary structure, Cassie's model treats the surface as a heterogeneous surface composed of air and the substrate material. The trapped air makes the surface more hydrophobic since the contact angle associated with air is 180°.

According to our knowledge of subwavelength optics and wettability, we propose a special type of structure which combines both antireflective and super-hydrophobic effects. First, the structure must be periodic and be at a subwavelength scale in order to guarantee the validity of the EMT method. Therefore, no scattering will be observed due to the periodicity. In addition, no high-order diffraction will be present if the period is smaller than the wavelength as diffraction orders other than the zeroth order are at the cutoff range. As for super-hydrophobicity, a periodic characteristic is also acceptable. For example, super-hydrophobic surfaces with periodic features were previously reported by Kim (Kim and Kim 2002) and Bico (Bico *et al* 1999). In addition, the subwavelength length scale approach has also been experimentally demonstrated,

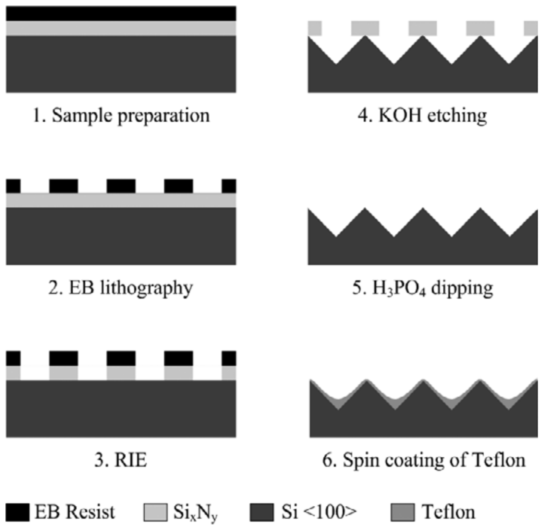

Figure 1. Fabrication process of the inverted pyramid structure.

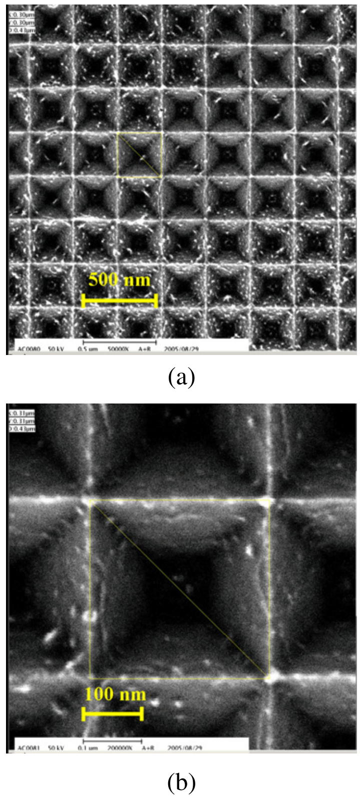

Figure 2. SEM photographs of the fabricated structure before Teflon coating: (a) 50 000× and (b) 200 000× magnification.

where the super-hydrophobic structures have characteristic scales ranging from 100 μm to less than 100 nm (He *et al* 2003, Nakajima *et al* 2001). Second, the profile and depth of the structure should be designed to create an equivalent GRIN surface, whose effective refractive index smoothly changes. Since depth determines the average slope of the index change, its depth must be deep enough. Typical values for the antireflective structure are of the order of the wavelength (Enger and Case 1983, Ono *et al* 1987, Raguin and Morris 1993, Kanamori *et al* 1999). This is also what super-hydrophobicity requires since a deeper depth increases the surface area and can trap more air. Third, the surface needs to be intrinsically hydrophobic, i.e. the intrinsic contact angle θ_Y should be greater than 90°. Even if the structure is not made of an intrinsically hydrophobic material, one can make surface modifications or coat a thin hydrophobic material on top of the structure so as to change the surface into a hydrophobic type while preventing the optical properties from changing significantly.

3. Experiments and calculations

3.1. Fabrication

We fabricated a specimen of an inverted pyramid structure to examine the combination of antireflection and enhanced hydrophobicity in a structure. Figure 1 shows the fabrication process, where a layer of 50 nm thick silicon nitride (Si_xN_y) was first deposited on a polished ⟨100⟩ silicon wafer as the mask of the wet etching. A 300 nm layer thick ZEP-520A electron beam (EB) lithography resist produced by the Zeon Corp. was then coated. It was followed by EB exposure using an EB lithography system (ELS-7500EX, Elionix Inc.) in order to define the periodic square pattern with a 300 nm period on the resist. After development and reactive ion etching (RIE), the pattern was transferred to the Si_xN_y mask. Afterwards, the specimen was dipped into 30% KOH at 70 °C for 1 min. Relying on the anisotropic etching rate of ⟨100⟩ silicon wafer, the wet etching process resulted in an inverted pyramid structure. To remove the Si_xN_y mask, the specimen was then dipped into H_3PO_4 at around 130–160 °C for 15 min. Figure 2 shows the scanning electron microscope (SEM) photographs of the fabricated structure at that particular stage.

Since silicon is intrinsically hydrophilic, a layer of hydrophobic material such as Teflon must be coated onto its surface to achieve the enhanced-hydrophobic effect. Dupont's Teflon AF1601, which is a solution of Teflon particles, was diluted to 0.4% using 3M's FC-40 solvent, which was spin-coated onto the specimen, followed by baking to form the desired Teflon film. An atomic force microscope (AFM) was used to view the topography of the structure (see figure 3).

3.2. Optical properties

For the inverted pyramid structure, the effective refractive index distribution versus depth was calculated by (1) and (2) as shown in figure 4. Although these equations only give the upper and lower limits of the effective refractive index, the trend of the curves demonstrates the gradual increase in the refractive index as the depth increases. In this calculation, the Teflon coating is not included. However, as can be seen in figure 5, our experimental results show no significant difference between the reflectivities with or without the Teflon coating.

The reflective spectra, shown in figure 5, were measured by a microscope (GX71, Olympus Corp.) with the reflected light guided to a spectrometer (S2000, Ocean Optics, Inc.). An objective lens of numerical aperture (NA) 0.5 was used for the illumination and collection. An aluminium mirror was used

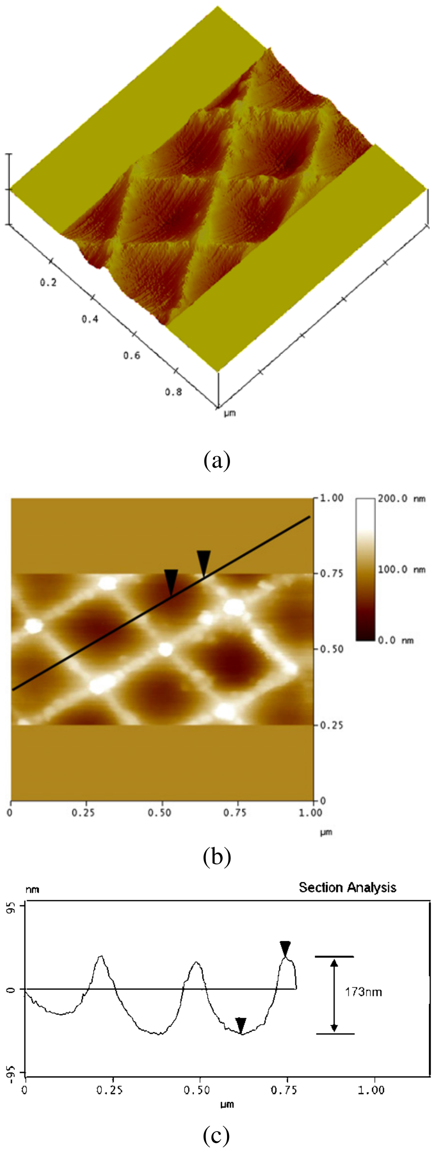

Figure 3. AFM topography data of the fabricated structure as shown in (a) 3D representation, (b) 2D representation and (c) line section.

as a reference and its reflectivity was taken as 0.91 over all wavelengths in the following data analysis.

In order to rigorously examine the antireflective effect and to obtain the precise optical properties, we used a commercially, available software called ANSYS to carry out the FEM simulations of the inverted pyramid structure (figure 6). The FEM simulation results agreed well with the experimental results. Clearly, both the experimental and simulation results show a reduction of the reflection from around 39% to 18% after the structure was imparted and which thus demonstrates an antireflection effect.

3.3. Wettability

We measured the contact angle using a VCA Optima Surface Analysis System (Advanced Surface Technology Products, Inc.). The droplet size used in this experiment was 0.5 μl. As shown in table 1, the smooth Teflon surface had an average

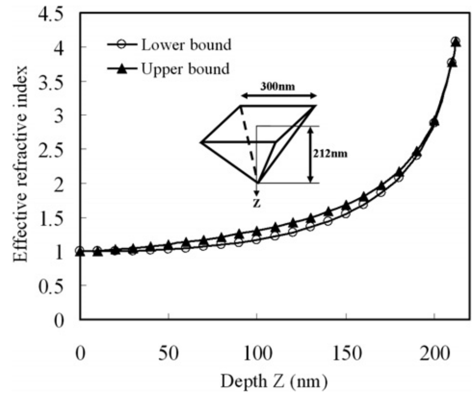

Figure 4. Effective refractive index distribution of the inverted pyramid structure which exhibits the GRIN behaviour. (Note: the Teflon coating is not included.)

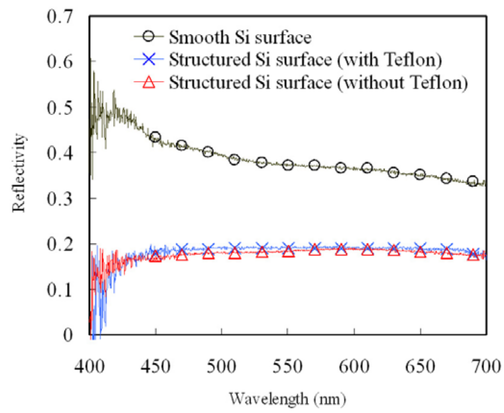

Figure 5. Experimental reflective spectra of the fabricated structure with and without Teflon coating and compared to a smooth bare silicon surface.

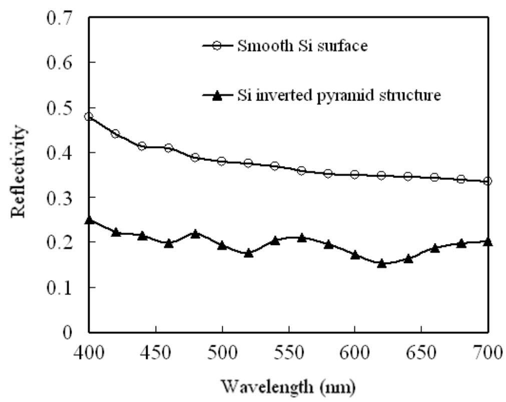

Figure 6. Reflective spectrum simulated by FEM for the silicon inverted pyramid structure (Teflon coating not included) and compared to a smooth silicon surface.

contact angle of 122.5°, and the structured surface showed an enhanced hydrophobicity as its contact angle increased to 135.9°.

For the crater-like structure such as the inverted pyramid used in this experiment, Wenzel's model is more likely to be

Table 1. Contact angles measured on a Teflon-coated smooth silicon wafer and on the Teflon-coated inverted pyramid structure. The measured value on the structure's surface is close to the theoretical value as calculated by Wenzel's model.

Surface type	Contact angle (deg)
Smooth silicon wafer coated with Teflon	122.5 ± 0.9
Inverted pyramid structure coated with Teflon	135.9 ± 1.5

applicable than Cassie's model since air is not easily trapped. By evaluating the surface area using AFM topography data, we obtained that the ratio r of (3) is 1.48, which corresponds to a theoretical contact angle of 142.7°. The contact angle obtained experimentally was 135.9°, which is close to the theoretical value.

4. Conclusions

In this paper, we proposed a special type of surface structure which combines antireflective and enhanced-hydrophobic effects. We examined the concept by fabricating an inverted pyramid structure. Experimental results and theoretical predictions of the structure agreed well. Our study demonstrates that the conflict between optical performance and wettability performance can be overcome as our newly proposed structure possesses both antireflective and enhanced-hydrophobic features.

Nevertheless, the antireflective effect, which reduced reflectivity from 39% to 18%, does not appear to be robust enough. Also, although the contact angle increased from 122.5° to 135.9°, the surface is not hydrophobic enough to be called super-hydrophobic. Further study and experimentation will need to be undertaken to obtain better results. The results can be improved as the performance of the inverted pyramid structure is mainly restricted by the fabrication technique used, where the anisotropic wet etching process limits the depth of the structure. More specifically, both optical performance and wettability performance can be significantly improved if the structure can be made to possess more surface depth.

Furthermore, the inverted pyramid structure used in this paper is only one example as other profiles which possess an effective index distribution similar to a GRIN surface can also exhibit antireflective features. Similarly, structures with structure profiles that can increase the surface area or trap air inside can enhance hydrophobicity (Chang 2004). Based on the above concepts, one can design structures with even better optical and wettability performance, especially since there are other more desirable structures for super-hydrophobicity since the inverted pyramid, which has a continuous three-phase contact line, is not desirable for hysteresis consideration (Oner and McCarthy 2000). In conclusion, a periodic subwavelength structure may be a solution to make highly transparent super-hydrophobic surfaces for such applications as window coatings and windshield coatings. Such structures can also be adapted to outdoor solar cells and LEDs to continuously keep the surface clean without sacrificing optical performance.

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