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Photo-Controlled Wettability Switching by Conformal Coating of Nanoscale Topographies with Ultrathin Oxide Films

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Here we explore the possibility of affecting the photoinduced wetting properties of nanostructures with tiny amounts of an inorganic modifier. Cicada wings are coated with a thin layer of ZnO by atomic layer deposition (ALD). We show that a few atomic layers of ZnO are sufficient to greatly modify the wetting properties. Our method only alters the surface chemistry, not the surface topography. Therefore the surface still exhibits high contact angles due to the pillars of the underlying cicada wing. At the same time, the wetting properties can be reversibly changed by UV light from nearly superhydrophobic to hydrophilic due to the ultrathin ZnO coating. We see that ALD has the potential to become a general method for modifying the photoinduced wetting properties of surfaces, keeping the topographical features of the original surface intact.

Introduction

Progress in new technologies often relies on our capability to expand the frontier of functional materials, which then would form an inspiring playground for those designing the next-generation devices. The current demand is definitely for multifunctional materials that can perform more than just one task at a time, and the most straightforward way to build up such materials is to intimately fuse two functional materials into a hybrid that yet carries the properties of both of its constituents. Indeed, there is a well-known category of highly useful metal/ceramics/polymer composite materials that are already playing central roles in the present high-tech applications. To further enrich the variety of hybrid materials in our hands we should not forget the possibilities provided by the nature around us. Biological materials are the product of millions of years of evolution, and often outperform man-made materials, for example, strong but lightweight spider silk, nacre, and self-cleaning Lotus leaves.[1−3] Inorganic modification of biological materials is a straightforward way to improve biological materials. For example, Knez et al. have greatly enhanced the mechanical properties of spider silk by adding tiny amounts of metal inclusions by atomic layer deposition (ALD).[3] Here we explore how tiny amounts of ZnO deposited by ALD modify the cicada wings to obtain stimuli-responsive wettability.

Surface wettability is an important property of a solid material, and it is affected both by the material's structure and chemical composition. By increasing the surface roughness and by lowering the surface energy, a material's water repellency can be enhanced. Nature provides us with a variety of materials with highly hydrophobic properties, including plant leaves, mosquito compound eyes, water strider legs, and insect wings. All these natural superhydrophobic materials have micro- and nanostructures, mostly coated by water repellent waxes. On the other hand, there exist various strategies to accomplish wettability conversion, that is, reversible change in contact angle by an external stimulus such as temperature, electric field, and light.[4] For example, certain semiconductive oxides, including TiO_2, ZnO, and SnO_2, change the contact angle by exposure to ultraviolet light.[5] After storage in the dark, the oxide becomes hydrophobic and the contact angle retains its original high value. In these inorganic oxides, the photogenerated formation of electron−hole pairs leading to oxygen-deficient surface sites is believed to be responsible for the effect. Hydroxyl group adsorption on the defect sites is preferred to oxygen adsorption, leading to low water contact angle. The original hydrophobic state is then restored as the hydroxyl groups are replaced by ambient oxygen during storage in dark.[6] The possibility to reversibly change the surface wettability from hydrophobic to hydrophilic state enables applications, for example, self-cleaning windows and liquid transport in microfluidic devices.

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In this work we explore the possibility of affecting the photoinduced wetting properties of biological nanostructures with tiny amounts of an inorganic modifier. Cicada wings were selected for the water repellent substrates. Cicada wings consist of hexagonally close-packed 250-nm high and 60-nm wide pillars. The distance between neighboring pillars is about 50 nm. As a result of the nanoscale array and the waxy coating of the pillars, cicada wings are extremely water repellent, and the water contact angle on a cicada wing surface exceeds 150°. The cicada wings were coated by ZnO using ALD, a thin film deposition method based on an alternate supply of gaseous precursors onto the substrate surface. As a result of the self-limiting growth mechanism of the method, films grown by ALD excellently follow the substrate surface topography and conformal films can be grown even on nanostructured surfaces.[7−10] However, an Al_2O_3 seed layer is needed prior to the deposition of the functional ZnO film to yield conformal growth on cicada wings. This is attributed to the waxy coating on the pillars of the wing nanostructure preventing chemisorption of the diethylzinc (DEZ) reactant and leading to area-selective film growth.[11] In addition, when reactive precursors are used, the film deposition can be carried out at relatively low temperatures enabling also the coating of temperature sensitive materials such as biological substrates. Successful ALD of ZnO has been reported at as low temperature as 90 °C,[12] and the growth-per-cycle is nearly temperature independent in the temperature range of 130−180 °C.[13]

Experimental Section

The sample preparation is to a large extent similar as described in reference 11. The cicada wings (*Pomponia intermedia*) were supplied from Thaibugs (Thailand). The cicada wings were first ultrasonically cleaned in acetone and deionized water. The wings were then coated by ALD in an ASM F-120 (ASM Microchemistry) ALD reactor at 1−3 mbar pressure. Nitrogen (99.999%, Schmidlin UHPN 3000 nitrogen generator) was used as a carrier and purge gas. A seed layer of Al_2O_3 was first deposited by using 20 cycles of trimethylaluminum (TMA; Witco GmbH) and water. Subsequently 10, 20, 30, 50, and 100 cycles of ZnO were deposited by using diethylzinc (DEZ; Crompton GmbH) and water. Both the Al_2O_3 and the ZnO depositions were performed at 120 °C. The metal precursor and water pulses were separated by equally long N_2 purge periods, and the pulse and purge times for Al_2O_3 and ZnO depositions were 2.5 and 2 s, respectively. The TMA, DEZ, and water precursors were evaporated by means of their vapor pressure from external reservoirs kept at 23 °C. Furthermore, Al_2O_3 and ZnO films were deposited on 5×5 cm^2 Si(100) and soda lime glass substrates for reference and thickness measurement purposes.

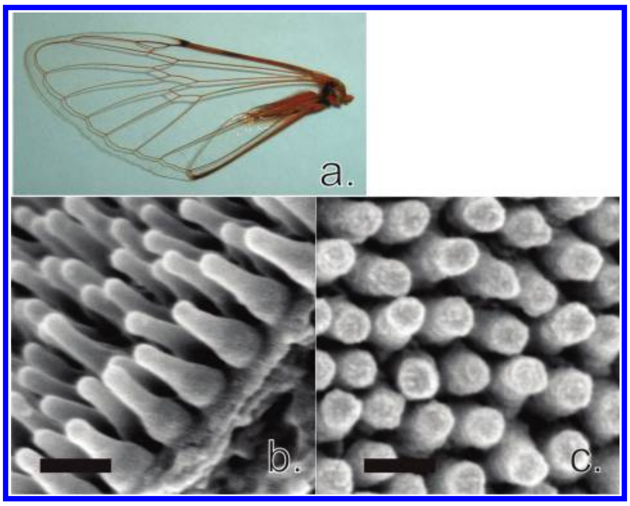

Figure 1. (a and b) Cicada wing and (c) cicada wings coated with inorganic film using ALD (20 cycles TMA/water +100 cycles DMZ/water). The scale bars are 200 nm.

The ZnO-coated wings were exposed for 60 minutes to ultraviolet light of 350 nm to study the photo-induced wettability change (Rayonet RPR-200 photochemical reactor). Water contact angles on cicada wings and on soda lime glass reference substrates were measured by a CAM 200 contact angle measurement system (KSV Instruments). The presence and amount of Zn deposited on the wings was confirmed by X-ray fluorescence (XRF) measurements with a Philips PW 1480 WDS equipment using Rh-excitation. The XRF measurements were performed in He atmosphere, and the data were analyzed with Uniquant 4.34 program utilizing DJ Kappa model for the determination of the compositions and mass thicknesses of thin film samples. Film reflectance and transmittance spectra were recorded with a Hitachi U-2000 UV/vis-spectrophotometer. Film thicknesses were determined from the reflectance spectra on Si(100) substrates by a spectrophotometric modeling method presented by Ylilammi and Ranta-Aho.[14] The transmittance spectra were measured from uncoated and ZnO-coated cicada wings to study their transparency in the 190−1100 nm wavelength range. The scanning electron microscopy (SEM) imaging of the cicada wings was performed with a LEO DSM 982 Gemini scanning electron microscope using 2 kV acceleration voltage. The wings were coated with sputtered platinum to enhance the image quality.

Results and Discussion

The growth-per-cycle values of our ALD processes for Al_2O_3 and ZnO at 120 °C were determined to be 1.0 Å/cycle and 2.0 Å/cycle, respectively, from experiments using Si wafers as substrate.[15] Hence, for a film made by depositing 20 cycles of Al_2O_3 and then, for example, 100 cycles of ZnO the total film thickness would be 22 nm. SEM images of the surface structure of an uncoated cicada wing and an Al_2O_3/ZnO-coated cicada wing are presented in Figures 1b and c, respectively. The diameter at the top of the uncoated pillars is about 60 nm. For the

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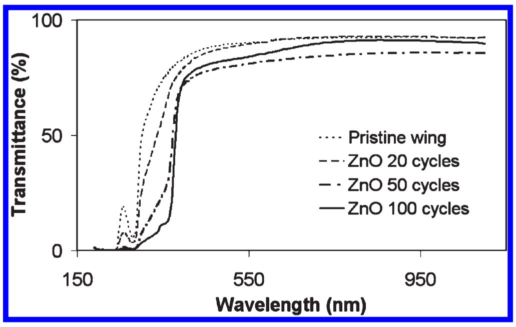

Figure 2. Transmittance spectra of pristine and ZnO-coated cicada wings in the 190−1100 nm wavelength range.

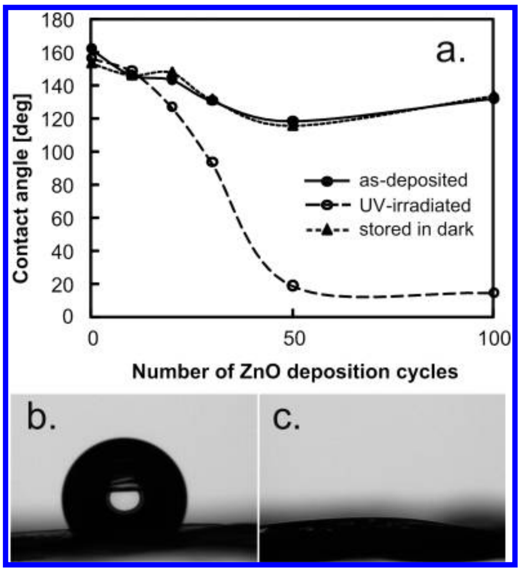

Figure 3. (a) Water contact angles of a pristine cicada wing and ZnO-coated cicada wings as a function of the number of ZnO deposition cycles. Water droplet on a cicada wing coated by 100 cycles of ZnO (b) before and (c) after UV illumination.

pillars coated with 20 cycles of Al_2O_3 and 100 cycles of ZnO, the total diameter is 100 nm. This corresponds to a thickness of 20 nm for the inorganic film. The film thickness on the cicada wing determined by SEM thus agrees well with the growth-per-cycle values obtained on Si wafers.

The coated wings were visually transparent and resembled the pristine wings. It is seen from the transmittance data in Figure 2 that the absorbance is increased in the UV region below 390 nm. Only minimal absorption due to ZnO coating was observed in the visible and near-IR wavelengths above 390 nm. Transmittance variations among different samples in the transparent spectrum range (390−1100 nm) are observed due to naturally shaded or flecked areas of pristine cicada wings.

The results of the water contact angle measurements are presented in Figure 3. The contact angle of an uncoated cicada wing is about 160°, and it changes only slightly when the wing is exposed to UV light. The 100-cycle ZnO film of approximately 20 nm in thickness deposited on the cicada wing leads to a contact angle of 132°, being significantly higher than the contact angle for a planar 100-cycle ZnO film on glass (determined to be 103°). Obviously, the peculiar topography due to the underlying cicada wing surface increases the contact angle of ZnO. Similarly, the topography also lowers the contact angle of ZnO after UV illumination. The contact angle of a 100-cycle ZnO film deposited on a planar glass substrate is 69° after UV exposure, whereas for a similar film on a cicada wing the UV exposure reduces the contact angle down to 14°. In all cases, after the UV exposure, the original hydrophobic state was achieved by dark storage at 100 °C within one hour. The lower contact angle of a ZnO-coated wing compared to that of an uncoated wing could be attributed to two possible factors: the ZnO coating may change the surface topography slightly but enough to decrease water contact angle and/or the surface energy of the ZnO coating may make it less hydrophobic than the original waxy layer on a pristine, uncoated cicada wing.

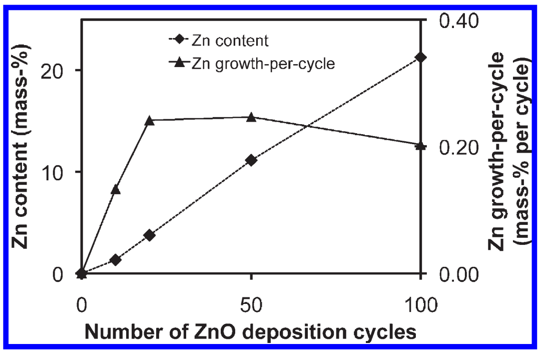

Figure 4. Zn content (in mass %; dashed line with diamonds) determined by XRF and its derivative curve (in mass % per deposition cycle; solid line with triangles) as a function of the number of ZnO deposition cycles.

We moreover investigated whether some threshold film thickness or threshold surface coverage is required for the ZnO film to allow the wettability conversion. A film of only 10 cycles of ZnO, corresponding to a thickness of 2 nm, did not show any change in the wetting properties by light exposure. The 50-cycle film showed the change in wetting properties similarly to the case of the 100-cycle film. The films with 20 and 30 cycles were intermediate. Furthermore, it was observed by XRF measurements that the initial growth-per-cycle of the thin ZnO layer is somewhat lower during the first 20 deposition cycles (Figure 4). The data indicate that full uniform surface coverage, possibly together with a minimum film thickness, is needed for the photoinduced wettability change to happen.

The light-induced wettability change is based on changing the surface functionality by light excitation at the bandgap of the semiconducting oxides. Photoinduced wettability change of TiO_2 and ZnO is typically realized on single crystals or on polycrystalline oxides, not on amorphous oxides. Also the ALD of the DEZ/water process is known to spontaneously lead to polycrystalline ZnO. In our experiments (Figure 3a) the photoinduced wettability became active only in films with a few tens of ALD cycles. This is likely attributed to an initial nucleation period of ZnO which is completed between 20 and 50 ALD cycles according to our XRF data. During this period the ZnO growth is slow, and island-like and nonuniform coverage is obtained.[16] Accordingly, part of the cicada wing surface may remain uncovered in our ZnO depositions up to say 30 cycles, thus leading to a lower than expected UV-tunable wettability effect. After some 50 cycles a full ZnO coverage is reached and a maximum UV-wettability effect is observed. The need for a threshold number of ALD cycles could also be due to a lower degree of crystallinity of the films at the initial stages of ALD. Note that the band properties of semiconducting oxides depend on the crystallinity.

Conclusion

In the present contribution we have demonstrated the possibility to combine a nanopatterned structure from nature with a functional property of an inorganic material. Conformal ultrathin films of ZnO were deposited by ALD on cicada wings to combine the superhydrophobicity of the wing and the UV-controlled wettability of ZnO, while keeping the good optical transparency of a pristine cicada wing intact. The property of photoinduced wettability change of ZnO was apparent in films that exceeded a critical surface coverage that equals a film thickness of approximately 4 nm. At the same time, the wettability property of the underlying nanostructured cicada wing surface was successfully transferred to the ZnO film grown on top of it such that the contact angle was clearly higher for the nonradiated ZnO film compared to a similar film on a flat surface, and similarly, the contact angle for a UV-radiated ZnO film was clearly lower compared to a similar film on a flat surface.

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