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Self-erasing and rewritable wettability patterns on ZnO thin films

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Self-erasing patterns allow a substrate to be patterned multiple times, or could store temporary information for secret communications, and are mostly based on photochromic molecules to change the color of the pattern. Herein we demonstrate self-erasing patterns of wettability on thin ZnO films made by atomic layer deposition. Hydrophilic patterns are written using UV light and decay spontaneously, i.e. become hydrophobic, or are erased aided by vacuum conditions or heat. We demonstrate that these patterns can be applied for channels to confine flow of water without physical walls.

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The control and guidance of droplets on a surface receives significant scientific and technological interest, for example in the field of microfluidics.¹ Spatial control of the wetting properties is typically achieved by a patterned surface chemistry, for example using self-assembled monolayers², or by a patterned surface geometry.³ Whereas writing of patterns in self-assembled monolayers usually is an irreversible process, other materials, like TiO₂ and ZnO semiconducting oxides, are appealing because of their reversible wetting characteristics.⁴ The photogeneration of a hydrophilic TiO₂ surface was first reported by Wang *et al.* in 1997.⁵ The wettability-conversion effects on the surfaces of ZnO and TiO₂ have been suggested to have similar reaction mechanisms.⁶ The structure of the surface has a major effect on the wettability properties. On a flat ZnO surface the contact angle (CA) of water was 109° in the hydrophobic state and changed to 5° with exposure to UV light in the experiments of Feng *et al.*⁷ However, for aligned ZnO nanorod films the contact angles were 160° and 0° in the hydrophobic and hydrophilic states, respectively.⁷ To improve the wettability properties, different kinds of nanostructured ZnO films have been prepared using various methods.^{8–13}

The irradiated hydrophilic surface returns to its original hydrophobic state with time in dark. Usually, full recovery requires several days of dark storage.^{7,14} According to Papadopoulou *et al.*¹⁵, thermal heating at 200 °C can be used to accelerate the recovery of ZnO to 1 h. The surface structure plays a role in the recovery process as well: For a surface with ZnO nanoneedles, it took about 60 h to be reconverted to the hydrophobic state, which is much less than the 250 h required in the case of nanorods.¹⁶ Also, ultrasonic treatment may speed up

the reconversion from hydrophilic to hydrophobic state on TiO₂ surface.¹⁷

One could utilize the self-erasing and rewriting ability of materials for storing temporary information as demonstrated by Grzybowski *et al.*¹⁸ in the case of metastable nanoparticle inks. Another potential application area of the wettability phenomenon is microfluidics, for example lab-on-a-chip devices. Surface energies play an important role when handling small volumes of fluids, and the photo-induced wettability provides a tool for controlling microfluidic systems. With such applications in mind, some research groups have studied hydrophobic-hydrophilic micropatterning.^{10,19–21} In contrast to the previous works, we demonstrate that the wetting patterns can be erased actively in vacuum conditions or spontaneously in ambient conditions. This self-erasing property allows for example construction of channels for one application and later making new channels with different design on the same substrate.

The ZnO films used in the experiments were deposited on glass and quartz substrates in a flow-type atomic layer deposition (ALD) reactor (F-120, ASM Microchemistry) at a pressure of 1–3 mbar.^{8,22,23} In the deposition, diethyl zinc (DEZ, Crompton GmbH) and deionized water were used as precursors. They were evaporated by means of their own vapor pressure and introduced in the reactor from external containers kept at room temperature. Nitrogen (99.999%; Schmidlin UHPN 3000 nitrogen generator) was used both as a carrier and purging gas. A single ALD deposition cycle consisted of 2.5 s long DEZ and water pulses separated by equally long nitrogen purge periods. The cycle was repeated 600 times at 120 °C substrate temperature to yield a uniform ZnO film with an approximate thickness of 100 nm. To improve the hydrophobicity of the surface, the films were stored in a high-vacuum oven (HVO) ($T \approx 60\text{--}130$ °C, $p < 10^{-7}$ mbar). In this work, flat ZnO surfaces were used, but ALD would allow modifying the wettability property through surface nanostructuring.⁸

We use an UV excimer laser to induce the hydrophobic-

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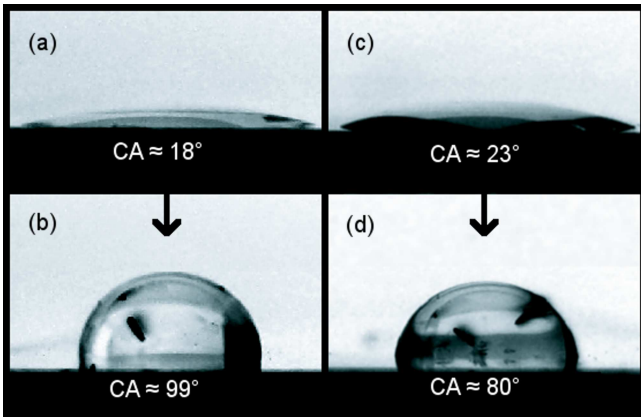


FIG. 1. Recovery of the hydrophobicity: a→b depicts the change in contact angle after 18 hours in a high-vacuum oven ($T = 75\text{--}130\text{ }^{\circ}\text{C}$, $p < 10^{-6}\text{ mbar}$), and c→d after 18-hours storage in a dark place at ambient conditions.

hydrophilic transition in ZnO. Similarly, Muir *et al.*²⁰ have used UV laser to change the wettability of lithium niobate and created micropatterns with interference-pattern exposure. In our work, the illumination of the films was done under ambient conditions with a Lambda Physik COMPex 205 KrF excimer laser, which produces 20–30 ns long pulses with a wavelength of 248 nm. The energy density of the pulses was controlled by a variable attenuator placed in front of the laser output and monitored by a calorimetric power meter. In order to pattern hydrophilic areas, the hydrophobic ZnO film was irradiated through a photomask placed on the sample. The photomasks were made by cutting a pattern into a piece of aluminium foil. The sessile-drop method was used to study the wettability properties of the films. The contact angles were determined from photographs taken of the droplets using a drop-analysis software.²⁴

The irradiation of a ZnO thin film on a glass substrate by UV laser pulses for 10 min induced a change in the contact angle of water from around 100° to less than 20° . The energy density of the laser pulses was approximately 17 mJ/cm^2 , and the repetition rate was 10 Hz. The irradiation was conducted in ambient laboratory conditions with a temperature $T \approx 20\text{ }^{\circ}\text{C}$ and a relative humidity $RH \approx 60\%$. Shortening the irradiation time to 5 min resulted in a contact angle of around 30° . Photographs of the sessile drops on the ZnO surface after the exposure to UV light are shown in Fig. 1a and c. The HVO was found to be the most effective method to wipe off the photoinduced hydrophilicity of the films. The contact angle of water on the ZnO film recovered to 100° after storage in the vacuum oven for 18 h as can be seen in Fig. 1a→b. Storage in dark at ambient conditions for 18 h partially restored the hydrophobicity to 80° (Fig. 1c→d).

Hydrophilic patterns were created on the hydrophobic ZnO surface using photomasks. Fig. 2a presents wetting of a simple hydrophilic cross which was patterned with an illumination time of 10 min. After the pattern-

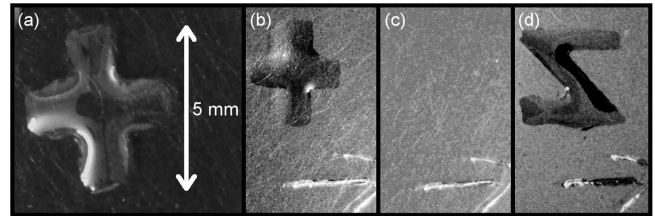


FIG. 2. Hydrophilic cross-shaped pattern on a ZnO film was illuminated with UV light. Dipping into water produced a wetting pattern (a,b). The pattern was erased by an HVO storage of 18 h after which no wetting was observed when dipped into water (c). Illuminating the same area for 450 s through a photomask with a different shape (here a mirrored letter Z) resulted in a new well-defined wetting pattern (d). The arrow at the bottom of the images is a scratch to denote that the images are all taken from the same location.

ing, the sample was dipped vertically into deionized (DI) water, and, as can be seen in Fig. 2a, water accurately follows the border between the hydrophilic area and the hydrophobic surroundings. The patterns can be erased and a new pattern can be illuminated on the film. The series of images in Fig. 2 shows how a cross-shaped wetting pattern (Fig. 2b) was erased with an HVO storage of 18 h. Dipping the sample into DI water after the storage did not create any wetting pattern (Fig. 2c). Illuminating the same area through a photomask with a different shape creates a new hydrophilic pattern, and dipping the sample into water results in a new, well-defined wetting pattern without any sign of the previous pattern (Fig. 2d).

Next, we demonstrate flow of water in a channel on the ZnO film with boundaries defined by the surface-energy. Hydrophilic lines were produced on two ZnO films by irradiating them through a $1 \times 18\text{-mm}^2$ photomask. A paper spacer of approximately $200\text{ }\mu\text{m}$ was placed between these ZnO-coated plates such that the hydrophilic lines were opposite to each other, and the plates were fastened with a clip. The experimental setup is depicted in Fig. 3a. When the end is dipped into water in a vertical position, a water column of approximately 12 mm in height rose in the capillary defined by the hydrophilic pattern (Fig. 3b). It shows that water can flow in a channel without physical walls but using surface energy as a barrier.

In addition to capillary forces, we show here that also centrifugal forces and gravity can induce flow in the channel without physical walls. Adding a droplet of water to the end of a hydrophilic line (Fig. 4a) and rotating the sample caused water to flow to the other end of the line (Fig. 4b). As can be seen in Fig. 4c and d, the drop on the hydrophobic surface remained in place during rotation. As demonstrated by tilting the sample, also gravity makes water flow from one end of the hydrophilic line to the other.

Importantly, the wettability contrast between the hydrophilic and hydrophobic areas starts to fade out imme-

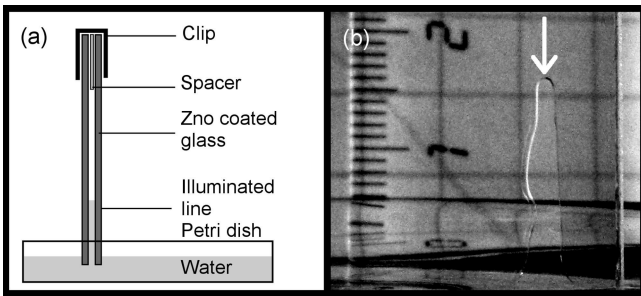


FIG. 3. Water column in a capillary defined by hydrophilic lines. The height of the column is approximately 12 mm. (a) Schematic illustration of the experimental setup. (b) Photograph of the water column with an arrow pointing to the column.

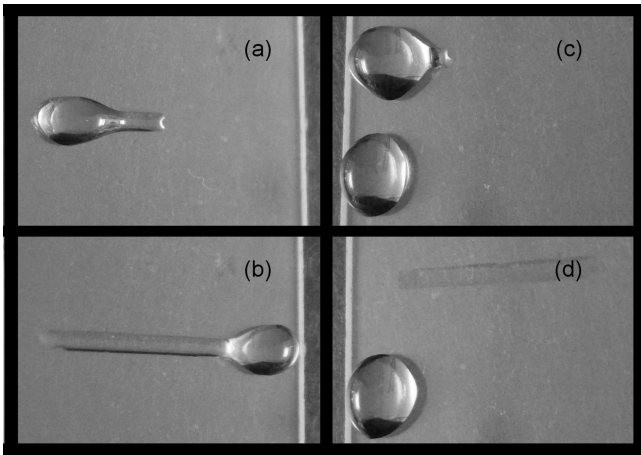


FIG. 4. Water flows in a channel ($1 \times 18 \text{ mm}^2$) due to centrifugal force when placed on a rotator. In photograph (a), a droplet of water is placed on the hydrophilic line. A clockwise spin of the plate causes water to flow to the other end of the line (b). Photograph (c) shows two droplets, one on the hydrophilic line and the other on hydrophobic surface. Here, a clockwise spin causes water to flow in the hydrophilic channel and, due to the high centrifugal force, out of the plate (d). On the other hand, the droplet on the hydrophobic surface remains totally motionless during the spin.

diately after the irradiation. When the irradiation was carried out with a laser-pulse energy density of 7 mJ/cm^2 for 10 min, approximately 30 min after the irradiation no selectable wetting was observed on the surface when dipping the sample into DI water. The wettability contrast, as well as the fade-out time for the pattern, can be controlled by the irradiation time and laser intensity. During the irradiation also the color of the ZnO film changes

slightly and recovers partially in contrast to the contact angle which recovers completely.

In conclusion, we demonstrate that planar ZnO films can be easily patterned by UV laser light into hydrophobic and hydrophilic areas. These hydrophilic patterns are sufficiently stable to allow wetting and flow of water in a channel without physical walls but confined by boundaries of low surface energy instead. Importantly, the hydrophilic patterns fade out, i.e., they become more hydrophobic, by vacuum conditions or spontaneously by storage in ambient conditions. This leads to loss of the wettable patterns. We foresee that the property of writing, self-erasing, and rewriting of hydrophilic patterns on robust planar inorganic films would allow applications towards reusable lab-on-a-chip and microfluidic systems.

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