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Surface morphology effects on the light-controlled wettability of ZnO nanostructures

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ZnO nanostructures of diverse morphology with shapes of corrals and cabbages as well as open and filled hexagons and sheaves prepared by APMOCVD technique, are investigated with water contact angle (CA) analysis. The as-grown ZnO nanostructures exhibit pure hydrophobic behavior, which is enhanced with the increase of the nanostructure's surface area. The most hydrophobic structures (CA = 124°) were found to be the complex nanosheaf, containing both the macro-and nanoscale features. It is concluded that the nanoscale roughness [contributes significantly](#) to the hydrophobicity increase. The character of wettability was possible to switch from hydrophobic to superhydrophilic state upon ultra violet irradiation. Both the rate and amplitude of the contact angle depend on the characteristic size of nanostructure. The observed effect is explained due to the semiconductor properties of zinc oxide enhanced by increased surface chemistry effect in nanostructures.

1. Introduction

Wettability is an essential property of solid materials, which is determined by the surface chemistry and the surface geometry. The wettability control is highly demanded for biological or microfluidic systems, where surface plays a key role for the mediation of solute or proteins adsorption and cell adhesion. For such applications, the materials with super-water-repellent or superhydrophobic surfaces (with a water contact angle more then 150°) are of interest. Smooth surfaces of low-energy-materials (i.e., fluorinated surface), known at present, typically provide the contact angle s up to 120°. However, the lotus leave demonstrates water contact angle as high as 160°, what is due to its special surface structure. Thus, the surface roughness plays an important role in determining the wetting behavior of solid surfaces. Moreover, morphology roughness affects not only hydrophobicity of the material: increased roughness of hydrophilic surface may favor the capillarity effect, resulting in efficient liquid incorporation into the nanostructured/nanoporous material. While, the dynamic modification of the wetting properties on these surfaces is still a challenging issue, the control of the wettability of different materials from superhydrophobic to superhydrophilic may be achieved via optical, magnetic, mechanical, chemical, thermal or electrical activations [1].

Recently, a reversible light-controlled hydrophobic/hydrophilic transition has been reported for zinc oxide (ZnO) films and nanostructures [2 - 12]. ZnO has direct wide band gap (~3.37 eV), high exciton binding energy at room temperature (~60 meV) and is optically transparent for visible light. It is therefore a prospective material for micro-, opto- and transparent electronics [13 - 22], for gas sensors [19], as well as transducer in biosensors [18]. Due to its non-toxicity, high chemical stability, and high electron transfer capability, ZnO is eventually a promising substrate for immobilization of bio-molecules [23].

As it has been suggested, via combining of fundamental semiconductor properties and a specific morphology, ZnO can provide highly hydrophobic surfaces, which may be changed to hydrophilic via irradiation with a light of energy more than the ZnO band gap (with a wavelength less than 375 nm) [2 - 12]. For the surface chemistry of ZnO, the reversible and tuneable wettability was explained to be the results of competition between the adsorption and desorption of surface hydroxyl groups and the organic chains rearrangement on the surface.

Furthermore, due to its highly developed surface the ZnO nanostructures are expected to exhibit more advanced controllable wettability including a faster hydrophobic/hydrophilic states transition and stronger contact angles contrast. ZnO has a large family of nanostructures; differing in shape, size and arrangement, including rods, pillars, wires, needles, belts, springs tetrapods etc [13 - 16]. Earlier, a number of studies were reported on the wettability of ZnO structures of different morphology: films [2 - 6], nanorods [7 - 10], nanoneedles [8], nanonails [8], and hierarchical structures [11, 12]. Since the wettability processes are surface mediated the nanostructures demonstrated more advanced wettability features, due to their highly developed surface. However, until now the effect of ZnO surface morphology - in terms of its nanosized features and microstructure is not explicitly clear, due to the number of separate data, collected from different samples and prepared by various techniques.

Here, we have studied the series of ZnO samples of evolutionary morphology – from plain ZnO surface and polycrystalline films to nanostructures of complex morphology. The effect of ultra violet irradiation on the wettability of the prepared samples has been studied: it is found that both the wettability change amplitude and hydrophobic/hydrophilic transitions time are affected by the morphology of the nanostructures. Particularly, complex nanostructures (ZnO nanosheaves) demonstrated the fastest time of wettability change: the contact angle was changed from 124° (highly hydrophobic) to 5° (superhydrophilic) after ~ 5 min. of UV irradiation. The observed effects are explained due to the significant enhancement of ZnO semiconductor properties by increased surface chemistry contribution in nanostructures.

2. Experimental details

The ZnO nanostructures were grown by atmospheric pressure metal organic chemical vapor deposition (APMOCVD) via using $\text{Zn}(\text{AcAc})_2$ as a solid state single source ZnO precursor. More details about the APMOCVD growth of ZnO nanostructures can be found elsewhere [24 - 26]. In order to obtain the intended morphology, the ZnO nanostructures have been grown at a variable precursor supersaturation at the substrate temperature ranged 200 – 500 °C. The precursor was loaded into an evaporator, and its pressure was controlled via changing the evaporator temperature (130 – 220 °C). Standard Si (100) substrates were used, being cleaned in acetone and ethanol for 10 minutes and dried by N_2 flow afterwards. The substrates were distanced from the evaporator and located in the deposition zone. Samples were located simultaneously in the growth chamber, being subjected to the existed temperature gradient in the growth zone. The growth chamber was pre-evacuated and filled by buffer Ar gas in a multi-step way. The total growth time was around 30 minutes.

The grown structures were characterized in terms of their crystal properties by X-ray diffraction (XRD) via θ - 2θ scans using a Philips PW 1825/25 diffractometer, utilizing Cu-K α radiation ($\lambda = 0.1542$ nm). The microstructure and morphology of the nanostructures were studied by scanning electron microscopy (SEM) using a Leo 1550 Gemini SEM operated at voltages ranging from 10 to 20 kV and using a standard aperture value of 30 μm . The wettability of the samples was characterized via static contact angle measurements, performed using a CAM 200 Optical Contact Angle Meter (KSV Instruments), using the sessile drop method. A 2 μl droplet of distilled deionized water was positioned on the surface via a microsyringe and images were captured to measure the angle, formed at the liquid / solid interface. The contact angle was calculated automatically via fitting experimental data by the software provided. UV light irradiation was realized in air ambient via exposure of the samples at certain time intervals by the low-pressure mercury lamp “Philips TUV PL_L18 W” of 18 W power maxima at wavelength $\lambda = 254$ nm. The reverse transition from the hydrophilic to hydrophobic state was performed via the storage in dark conditions at room temperature. Bulk ZnO single-crystal from ZnOrdic [27] has been used for a comparison for wettability analysis.

3. Results and discussion

3.1 Morphology diversity of ZnO nanostructures

Figure 1 shows the different ZnO nanostructures that were prepared at a temperature range 200 – 500 °C. According to the applied growth procedure, the surface morphology has been changed in its microscale as well as in terms of its nanosized features. Within the temperature range the nanostructures undergo an evolution of its shape from polycrystalline blocks of grains (Fig. 1a) to the complex structures of microscaled bundles of nanosized needles - nanosheaves

(Fig. 1f). A distinctive feature is that the surface morphology changes according to the growth temperature, being driven by ZnO crystal planes anisotropy, as will be discussed below. The XRD analyses revealed that all these samples are a single-phase ZnO. Only distinctive reflections of the planes $(10\bar{1}0)$, $(10\bar{1}1)$, and (0002) were observed from the $\theta - 2\theta$ spectra of the samples. As it is demonstrated in the Table 1, the (0002) texture became dominating with the temperature increase. This is expected from the difference in the surface free energies for the main crystallographic planes of hexagonal ZnO: $G_{001} = -2.8102$ kJ/mol, $G_{101} = -2.1067$ kJ/mol, and $G_{100} = -2.0013$ kJ/mol, preferential growth on the plane of lowest energy – (001) is favoured [28]. More details on the structural properties of the samples are described in Ref. 28.

Fig. 1 SEM images of ZnO nanostructures as a function of growth temperature (T_{gr}): a) corals ($T_{gr} = 200 - 240$ °C), b) cabbages ($T_{gr} = 240 - 280$ °C), c) porous hexagons ($T_{gr} = 280 - 320$ °C), d) bundles ($T_{gr} = 320 - 365$ °C), e) sheaves ($T_{gr} = 365 - 440$ °C) and f) open sheaves ($T_{gr} = 440 -$

550 °C). The insets show contact angle images from droplet experiments for the respective as-grown samples.

An increase in growth temperature first causes a change of the morphology of ZnO nanostructures: the corals sample with a grain size around 1 – 2 μm , consisting of nanoscaled blocks 120 – 100 nm of size are transform into the cabbage-like structures with a lateral size 1.5 – 2 μm , containing the nanopores of size $\sim 100 - 90$ nm (Fig. 1b). With temperature increase up to 320 °C the morphology undergoes further transformation into porous hexagonal crystals of approximately the same lateral size on the microscale, that are directed perpendicular to the substrate plane. Hexagons still contain the pores of characteristic size $\sim 90 - 80$ nm. The origin of pores we explain as due to increased growth rate along the walls, which are apparently c-axis oriented. As one can see, the pore size increases within the temperature range (240 – 320 °C), while the walls between the pores are narrowing. Finally, the microstructure evolution switch into the nanoscale: the walls transform into rods or needles, emanating from the common root (Fig. 1d-f). On the microscale, the needles are arranged into bundles, while maintaining a hexagonal geometry (Fig. 1(d)). A further temperature increase turns the bundles of nanoneedles into the sheaves with a nanoneedle tip size $\approx 60 - 45$ nm, which are finalized by the open sheaves with the smallest feature size $\approx 45 - 30$ nm of tip diameter. Open sheaves are created under decreased density of bundles and the needles in the open sheaves loose their mutual hexagonal arrangement. It may be imagined as by increasing the distance between needles – thus, the sheaves are opening.

Fig. 2 SEM profile view of complex ZnO nanostructures (ZnO nanosheaves) (a): Si substrate is covered by thin polycrystalline layer, followed by ZnO nanopillar's growth; further growth the ZnO pillar is continued as the bundle of ZnO nanoneedles (diameter $\approx 45 - 30$ nm and length around 3 μm) (b).

The relationship between the obtained morphology and the deposition conditions has been reported recently [29]. First the ZnO polycrystalline layer is deposited, consisting of grains, which are differently oriented toward the substrate surface. Via increase of the growth temperature at this stage, the number of grains oriented with their c-axis perpendicularly toward the substrate is increasing such that the (0002) texture is promoted. Second, via depleted growth conditions, the selective growth of the (0002) oriented grains is achieved, providing further growth the ZnO pillar on their apex. Finally, the rapid increase of the growth rate results in multi-nucleation on the top of every pillar, which continues with wall formation (in the case of cabbage-like and hexagon's morphology), and nanosheaves formation at elevated temperatures (bundles and sheaves). Our obtained ZnO nanosheaves (Fig. 2a,b) are very similar to the earlier described “micronanobinary structures”, which have been theoretically motivated by Zhang to be extremely efficient as hydrophobic surfaces [9]. The nanosheaf structures are in fact micro-sized bundles of tiny ZnO nanoneedles with their average diameter around 30 nm and length up to 3 μm . The distance between nanowires in a bundle was found to increase during growth away from their roots.

Further increase of the growth temperature (over 550 °C) caused the deterioration of the ZnO nanostructures microstructure and worsening of the tips surface morphology, what can be due to possible ZnO species re-evaporation at elevated deposition temperatures. The temperature evolution of ZnO nanostructure morphology along with wettability characteristics of as-grown samples is presented in Table 1.

3.2 Surface morphology effect on the wettability of ZnO nanostructures

As it was suggested above, since the wettability processes are surface mediated, the surface roughness may amplify the present wettability character. Via surface roughening of the hydrophobic state material the super hydrophobicity can be reached. We have analyzed the wettability of the ZnO nanostructures via measuring of the static contact angle (insets in the Fig. 1a-f). As expected, the as-grown structures represent a hydrophobic surface: all the samples demonstrated the hydrophobic behaviour with a contact angle θ_b ranging from 90 to 124° (See Table 1).

Fig. 3 SEM profile images of the ZnO bulk crystal (a) and the ZnO nanostructure (open nanosheaves sample) (b). The insets represent the schematic drawing of the relevant Wenzel or Cassie-Baxter models of wettability.

The wettability processes on ZnO surfaces can be considered according to the Wenzel or Cassier-Baxter models (Fig. 3) [30 - 31]. For a liquid drop on a *smooth* solid surface, the Young contact angle θ is determined by the surface free energies involved [32]:

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \quad (1)$$

where γ_{sv} , γ_{sl} and γ_{lv} are the solid/vapor, solid/liquid, and liquid/vapor tensions, respectively. The change from smooth single-crystal surface to polycrystalline films etc. is accompanied by an increase of the surface roughness, which is defined as the ratio of the actual over the apparent surface area. According to the Wenzel model [30] the apparent contact angle θ for a *rough* surface is given by:

$$\cos \theta = r \cdot \cos \theta_b \quad (2)$$

where θ_b is a contact angle on a smooth surface (before the UV irradiation) and r is a surface roughness factor. r affects the hydrophobicity via changing the surface roughness while keeping the indissoluble contact between surface and water. Once the contact is lost, the Cassier – Baxter state is applicable, which can be described by the Cassier equation [31]:

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (3)$$

where θ_r and θ are the contact angles for rough and smooth surfaces, respectively; f_1 and f_2 are the fractional interfacial areas of ZnO and the air trapped between the surface and a water droplet, respectively. Apparently, a larger air fraction f_2 yields a more hydrophobic surface [9].

It was reported [9], that the wettability of a surface can be enhanced by increasing the surface roughness within a special size range, because the air trapped between the solid surfaces and the water droplet can minimize the contact area. Thus, the structures, which are rough on *both* micro- and nanoscale (so called “micronanobinary structures” [9]) are the most promising for reaching the highly hydrophobic surfaces. It is evident, that both the microstructure and nanostructure can change the surface roughness, but which one is more influential for hydrophobicity is not clear.

Fig. 4 Water contact angle (θ) of the as-grown ZnO nanostructures: the effect of the micro- and nanoscaled roughness (R and r) on the contact angle values. The lines are guides for the eye.

Fig. 5 (a) - Change of the contact angle (θ) with time upon UV irradiation for ZnO of diverse morphology; the respective transitions super hydrophobic and super hydrophilic are shown; the lines are just guides for eyes; (b) – Rapid wettability change from highly hydrophobic to superhydrophilic for ZnO nanosheaves; the insets are wettability images before irradiation (top) and after 5 min of UV irradiation (bottom).

In order to distinguish the influence of micro- and nanoscaled roughness separately on the surface hydrophobicity, we introduced the coefficients R and r as micro- and nano-scaled surface roughness, respectively, defined as the ratio of height to the diameter of the features on the surface. The estimated values of R and r for the nanostructures are presented in the Table 1. As one can see, the micro- and nanoscaled roughness are changed mutually with the temperature increase (Fig. 4). Moreover, there is a clear correlation between the R and r behaviour and the contact angle. First, the increase of the growth temperature (for corrals, cabbages and porous hexagons) causes the micro scaled roughness R to be enhanced. This results in a moderate increase of the contact angle from 91° (for bulk crystal) to 103° for cabbages-like structures. At the same time, r is rather constant within this range. However, it starts to increase rapidly with the further temperature increase (for bundles, sheaves and open sheaves), while the micro roughness stay rather constant. An increase of the nanoscaled roughness causes more prominent contact angle increases from 104 up to 124° .

Thus, we can conclude, that the complex surface morphology, based on micro- and nanoscaled features does provide the mostly hydrophobic surface.

3.3 UV irradiation effect on the wettability of ZnO nanostructures

In order to change the wettability character of ZnO, we irradiated the as-grown structures and a reference ZnO bulk sample by ultra violet (UV) light of wavelength 254 nm, which provides the photon energy larger than the ZnO band gap (~ 3.37 eV). The irradiation time was varied from 2 to 30 minutes and the wettability of the samples was measured every 5 minutes (Fig. 5). After the UV irradiation the wetting transition from hydrophobic to hydrophilic state occurs for all the samples, including bulk ZnO (Fig. 5a). This is due to the semiconductor nature of ZnO and similar effects have been observed for other materials (e. g., TiO_2 [33, 34]).

The change of the wettability character can be explained by the following mechanism: via irradiation by the UV light with photon energy, higher than or equal to the band gap of ZnO, the electrons (e^-) in the valence band are excited to the conduction band. The same number of holes (h^+) are simultaneously generated in the valence band:

Some of the holes react with lattice oxygen (O^{2-}) to form surface oxygen vacancies $\text{O}^{\cdot-}$ (surface trapped hole), while some of the electrons react with lattice metal ions (Zn^{2+}) to form Zn^+ defective sites (surface trapped electrons):

Water and oxygen may compete to dissociatively adsorb on these defective sites. The surface trapped electrons (Zn_s^+) tend to react with oxygen molecules adsorbed on the surface:

At the same time the water molecules may coordinate into the oxygen vacancy sites (V_o), which cause the dissociative adsorption of the water molecules on the surface. The defective sites are *kinetically* more favorable for hydroxyl groups (OH^-) adsorption than oxygen adsorption. It promotes increased water adsorption on the irradiated ZnO surface. Thus, the hydrophilicity of the ZnO surface is greatly improved and the water contact angle is drastically reduced [34].

The above described mechanism of wettability change is applicable to both bulk and nanostructure samples. Moreover, for complex nanostructures, which contain both the micro- and nanoscaled features, a few additional collisions exist. First of all, the specific arrangement of the nanostructures plays a significant role in the effect observed. During the UV irradiation the change of the hydrophobic to hydrophilic state is followed by the change of the Cassie - Baxter state to the Wenzel state. Since the air pockets are no longer thermodynamically stable, the liquid begins to penetrate the nanostructures from the middle of the drop, creating a “mushroom state”. Such a feature promotes the hydrophilicity of the surfaces of the ZnO nanostructures. Moreover, the water penetration front propagates to minimize the surface energy until it reaches the edges of the drop, thus arriving to the Wenzel state. Next, the water drop is spreading further beyond the drop. The film smoothes the surface roughness and the Wenzel model no longer applies. This explains the superhydrophilic state, which has been achieved for the ZnO nanostructures.

Thus, all the complex nanostructures demonstrate the superhydrophilic behaviour after a certain period of time. However, the time necessary for the transition from hydrophobic to superhydrophilic surface was found to be depended on the morphology of the samples. It is clearly seen that as small are the surface features the smaller is the wettability state transition time (Fig. 5a). The most rapid transition from the hydrophobic to hydrophilic state was observed for

ZnO open sheaves – after as short as 5 minutes of the irradiation the contact angle has been changed from the highest value $\theta_b = 124^\circ$ to as low as $\theta_a = 5^\circ$ (Fig. 5b). We explain such a velocity due to the lowest nanoneedles diameters (Fig. 2b) and respectively their high surface area. Hence, in such a structure surface mediated processes are amplified. Since the contact angle change under UV irradiation is a result of the photocatalytic reaction on the ZnO surface, small features and respectively high surface area, are determining this effect. For nanosheaves, the exposed surface area is largest and the photo-catalytic processes affect the surface faster than for the other samples. The importance of the nanostructured morphology is confirmed by the fact, that the lowest contact angle after UV irradiation for the ZnO bulk was $\theta_a = 30^\circ$ independently of the time of irradiation.

According to the above described mechanism, the induced super hydrophilic state in ZnO is unstable with time and may return to the initial hydrophobic state after a while. This is because at the hydrophilic state - after the hydroxyl adsorption, the surface becomes energetically unstable. Because oxygen adsorption is *thermodynamically* favored, oxygen is more strongly bonded on the defect sites than on the hydroxyl groups. Consequently, the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms when the UV-irradiated films were placed in the dark. Heat treatment can accelerate the elimination of surface hydroxyl groups [34]. As a result, the surface reverts back to its original state (before UV irradiation) by means of dark storage (or heat treatment), and the wettability is reconverted from hydrophilicity to hydrophobicity again [35]. We did not apply heating or other actions in order to stimulate the reconvert of the ZnO surfaces from hydrophilicity to hydrophobicity. The samples were stored in dark ambience at room temperature. After a few days the samples possessed the same hydrophobic behavior as the as grown. Such a long recovery time can be explained by the porosity of the samples, through which water entered during the hydrophilic state.

4. Conclusions

The effect of surface morphology on the UV light-controlled wettability of ZnO nanostructures has been investigated. It is observed that the degree of the hydrophobicity – what is common for as-grown ZnO – can be increase via roughening of the surface morphology. A correlation exists between increasing of the both micro- and nanoscaled roughness and enhancement of the ZnO hydrophobicity. The highest degree of hydrophobicity is exhibited by complex ZnO nanostructures, containing both micro- and nanoscaled surface features.

The hydrophobicity state of the studied ZnO nanostructures was found to be easily converted to superhydrophilicity after UV irradiation during a certain time (~5 - 30 min). This is

explained by the semiconductor nature of ZnO and its surface chemistry. However, the time of hydrophobic/hydrophilic transition depend strongly on the surface morphology – smaller ZnO features on the surface yields a faster hydrophobicity-hydrophilicity transition. The fastest and most prominent wettability change is obtained for ZnO nanosheaves: the contact angle changes from 124° to 5° after ~ 5 min. of irradiation. Such effect is explained to be due to the essentially small needles diameter (around 30 nm at the tips) and their highly developed surface area.

The results obtained encourage the application of the ZnO nanostructures with controllable wettability, particularly for the effective control of micro or nano-fluid motion and respectively, enabling patterning hydrophilicity/hydrophobicity with photolithography. This might be useful for rapid prototyping of microfluidic systems. In a more far perspective the observed features of ZnO can be used for the design of microdevices, where the nature of a surface plays a key role on the mediation of protein adsorption or cell adhesion.

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