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Light-induced reversible hydrophilicity of ZnO structures grown by aqueous chemical growth

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ABSTRACT

ZnO wurtzite microrods and flowerlike structures were deposited on glass and ITO substrates by the aqueous chemical growth (ACG) technique at mild temperature (95 °C). Wettability studies revealed that the as-deposited structures are hydrophilic and super-hydrophilic for short and long growth times, respectively. The hydrophilic ZnO surfaces could be reversibly switched to super-hydrophilic by alternation of UV illumination and dark storage. Our results demonstrate that ACG at low temperatures can be efficiently employed to deposit transparent photosensitive ZnO structures exhibiting reversible wettability changes.

1. Introduction

The control of the wettability of the films depends significantly on both the surface energy and roughness and it is very important in many aspects of daily life, including industry and agriculture [1–3]. For various practical applications, both highly hydrophobic [1,4] (water contact angle larger than 150°) and highly hydrophilic [5] (water contact angle smaller than 10°) coatings are desirable and various materials have been proposed and studied towards this scope.

Among other materials, the wetting properties of metal oxides, mainly of TiO_2 and ZnO, have been widely studied, since irradiation with UV light may significantly modify their wettability [6,7]. This photo-induced transition can be reversed after storage in the dark, indicating self-cleaning characteristics. Besides this, recent studies revealed that microstructures and nanostructures exhibiting hierarchical roughness can be highly hydrophobic [8,9]. Especially, metal oxide structures have been reported to be reversibly switched between super-hydrophobicity and super-hydrophilicity [10], opening the way for the construction of the future-generation of smart, self-cleaning surfaces [5]. Comparing various oxides and their wetting properties, one can easily notice the ability of ZnO to form microstructures and nanostructures using various methods as well as its advantageous characteristic to transform from rods [10,11] to columns and wires [12].

In the present work we investigate the wetting properties of ZnO microstructures under the effect of UV irradiation. The ZnO structures of various sizes and shapes were synthesized using the ACG technique, which is a novel, simple, environmental-friendly and inexpensive method for depositions at mild temperatures, firstly reported by Vayssieres [13]. More specifically, the photo-induced reversible wetting properties of ZnO wurtzite structures deposited on glass and ITO substrates at low temperatures were studied, in relation to deposition time and the resultant morphological characteristics.

2. Experimental details

ZnO structures were grown by ACG on both glass and ITO substrates using an equimolar (0.01 m) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) as a precursor [14]. The solution was placed on

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Pyrex glass bottles with autoclavable screw caps, with the substrates positioned on the bottom, and heated at 95 °C for 1, 2, 5 and 10 h, respectively. After each induction time, the substrates were thoroughly washed with MilliQ water to eliminate residual salts or amino complexes, and dried in air at the same temperature (95 °C). Before deposition, all substrates were ultrasonically cleaned with spectroscopic grade propanol and acetone, washed with MilliQ water and dried under N_2 gas flow. The crystal structure of the ZnO structures was determined by X-ray diffraction (XRD) using a Rigaku diffractometer with Cu $K\alpha$ X-rays. Room temperature optical transmittance of the ZnO structures was recorded in the wavelength range 190–800 nm using a Perkin Elmer (Lambda 950) spectrometer, while their surface morphology was observed by a JEOL Scanning Electron Microscope (SEM). Finally, the surface wettability of the ZnO structures was evaluated by water contact angle measurements performed by the sessile drop method. A 10 μl Millipore water droplet was gently positioned on the surface of the samples using a microsyringe. A CCD camera-lens optical system was used to capture digital images of the droplet profile from a location parallel to the substrate. Contact angles were subsequently determined from the corresponding pictures using an image-processing algorithm, and a mean value was calculated from at least five individual measurements. Light-induced hydrophilicity was evaluated in atmospheric air and a temperature of 25 °C by irradiating the samples at certain time intervals using a Hamamatsu Hg lamp, centered at 365 nm, with an intensity of 4 mW cm^{-2} at the position of the samples. After each irradiation period, a 10 μl water drop was placed on the irradiated area and the corresponding contact angle was measured again. Following irradiation, the samples were stored in the dark at room temperature and then the respective contact angles were measured again. Each characterization method was completed on at least three samples prepared under the same conditions for consistency and reproducibility.

3. Results and discussion

Fig. 1 presents SEM micrographs of the ZnO structures formed on glass and ITO substrates for various growth times. For both substrates, we observe that depending on the growth time, rods or flower-like structures of various sizes are deposited and the macroscopic surface roughness increases with increasing deposition time. For 1 h growth (see Fig. 1(a) and (d) for glass and ITO substrates, respectively), rods are mainly formed with a length of about 2–3 μm and a diameter of ~500 nm. However, only a partial coverage of the substrate area (~30%) could be achieved due to the initial stage of the growth. For 2 h growth, the rods become bigger, their length ranges from 2 μm to 5 μm with a diameter of about

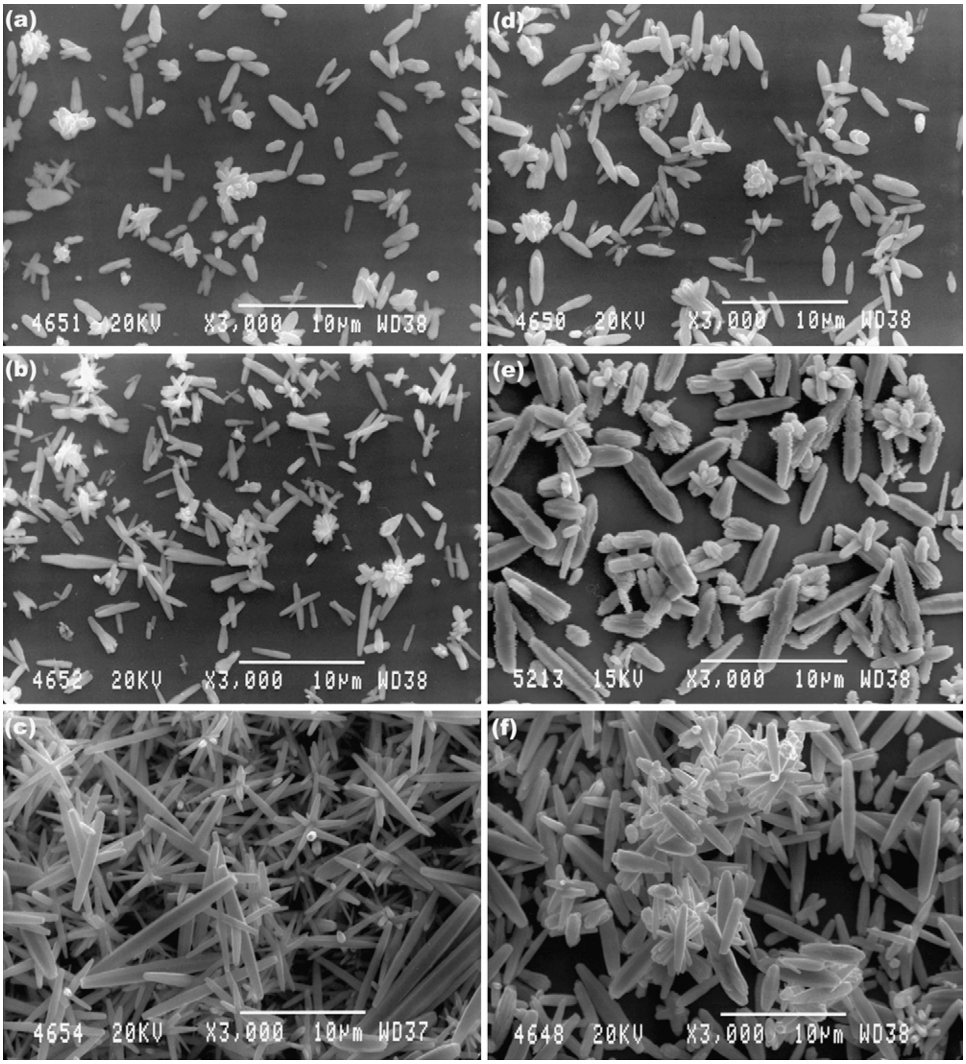

Fig. 1. SEM images of ZnO structures grown by ACG at 95 °C on glass for 1 h (a), 2 h (b) and 5 h (c) (representative for 10 h) and on ITO for 1 h (d), 2 h (e) and 5 h (f), respectively.

500–800 nm. Moreover, the microscope glass coverage reaches 60% (see Fig. 1b), while for the case of ITO, it is almost 75% (Fig. 1e). For longer growth times (5 h), the ZnO rods further develop on glass (length ~10 μm, diameter ~1 μm) with a substrate coverage of about 85% (see Fig. 1c), while many flower-like structures are also present. On the other hand, the ZnO structures grown on ITO substrates for 5 h are more uniform, consisting mainly of single microrods and only few flower-like structures, having a typical diameter of about 1 μm and length of several microns (~7–8 μm). Finally, when the growth time reaches 10 h, the flower-like architectures dominate, resulting in substrate coverage of almost 90%. These flower-like structures consist of uniform microrods with a typical length of about 10–12 μm and a diameter of ~1 μm.

The ZnO structures deposited on both glass and ITO substrates exhibit sharp diffraction peaks, characteristic of the ZnO wurtzite hexagonal phase (wurtzite-type, space group $P6_3mc$, JCPDS card file no. 36–1451), which implies that pure ZnO was formed only. No characteristic diffraction peaks from other phases or impurities were detected. For the 1 h and 2 h growth, only the first characteristic peak of ZnO can be clearly present (i.e. the (1 0 0) direction) irrespective of the type of the substrate. The same XRD pattern stands for the case of ZnO structures grown on ITO substrates for 5 h (see Fig. 2b), while for 5 h growth on glass, all the peaks attributed to the wurtzite ZnO structure are revealed (see Fig. 2a). Furthermore, for 10 h growth on both glass and ITO substrates all the characteristic diffraction peaks of ZnO are noticeable (see Fig. 2c). Regarding the mean crystallite size (d) of the ZnO structures, this was determined using the (1 0 0) peaks and the Debye–Scherer formula. The determined values range from 40 to 46 nm for 1 h and 10 h, respectively, regardless the substrate.

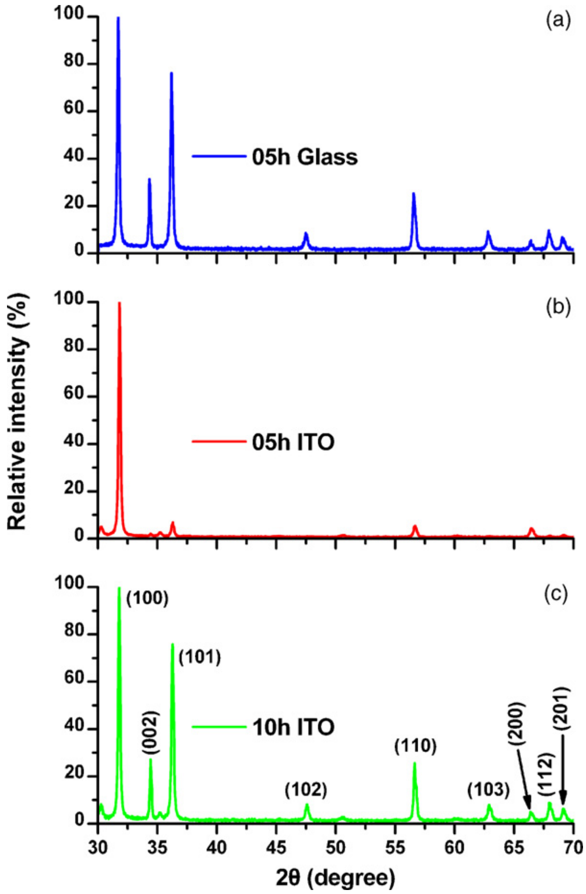

Fig. 2. XRD patterns of ZnO structures grown by ACG at 95 °C: (a) on glass for 5 h, (b) on ITO for 5 h and (c) on ITO for 10 h, respectively.

Transmittance measurements showed that all the samples for short deposition times (up to 2 h) were quite transparent in visible spectra region, the corresponding transmittance being around 60% for glass and 55% for ITO substrates, respectively. These values suggest that the films scatter the light as expected from their granular microstructure (see Fig. 1). For longer growth periods (5 and 10 h), the transmittance reduces significantly due to the increase of both the coverage of the substrates and the average thickness of the ZnO samples.

Fig. 3a, c, e, and f show wetting angle images for un-irradiated as-deposited structures while in Fig. 4, the corresponding contact angles of the structures and the substrates are presented. In the as-deposited un-irradiated state, all samples grown for time periods 1 h or 2 h on either glass or ITO substrates exhibit hydrophilic behavior, the corresponding water contact angles being always similar (glass) or lower (ITO) than that of the substrate. In contrast, samples grown for 5 h and 10 h consisting of combination of single rods and flower-like structures are superhydrophilic, exhibiting near-zero contact angles. Water droplets spread significantly after being positioned on the samples, while the final shape of the water stain is not circular, probably due to high surface roughness.

It is well known that the wettability of a film is a synergy of its surface roughness and crystallinity. XRD patterns (see Fig. 2) show that the crystallinity does not change appreciably among the grown films upon increasing the growth time. All films exhibit the ZnO wurtzite hexagonal phase, indicating that only pure crystalline ZnO is formed. We therefore suggest that the variation of the initial contact angle among samples grown should be primarily attributed to the difference in their surface roughness.

In order to understand the response of the as-deposited un-irradiated structures, we have to consider the effect of the macroscopic surface roughness on the wettability, which has been theoretically approached by two different models. In the Wenzel model [15], the water drop is assumed to wet the entire rough surface, not leaving any air pockets. Then, the observed water contact angle, θ_W, is given by the following equation:

$$\cos\theta_W = r\cos\theta \qquad (1)$$

where r is the ratio of the unfolded surface to the apparent area of contact under the droplet, and θ is the contact angle on a flat surface of the same nature as the rough one. Since r is always greater than unity, this model predicts that the contact angle of a liquid that wets a solid ($\theta < 90^\circ$) decreases when its surface is roughened ($\theta_W < \theta$), while, roughening a non-wetting flat surface ($\theta > 90^\circ$) always increases its hydrophobicity ($\theta_W > \theta$). Therefore, the Wenzel's model predicts enhancement of either non-wetting or complete wetting with increasing roughness. In contrast, Cassie and Baxter [16] assumed that the liquid does not completely permeate the roughened solid. As a result, air pockets are trapped inside the features underneath the liquid, which sits above a composite surface made of solid and air. For a Cassie–Baxter drop, the contact angle, θ_{CB}, is an average between the value on air (that is, 180°) and on the flat solid (that is, θ) and is given by:

$$\cos\theta_{CB} = -1 + f(1 + \cos\theta) \qquad (2)$$

where f defines the fraction of the projected solid surface that is wet by the liquid. As f is always lower than unity, this model always predicts enhancement of hydrophobicity only, independent of the value of the initial contact angle θ. In summary, it can be anticipated that the complete wetting predicted by Wenzel's equation will occur only if the surface texture can be completely penetrated by the volume of the deposited droplet [17].

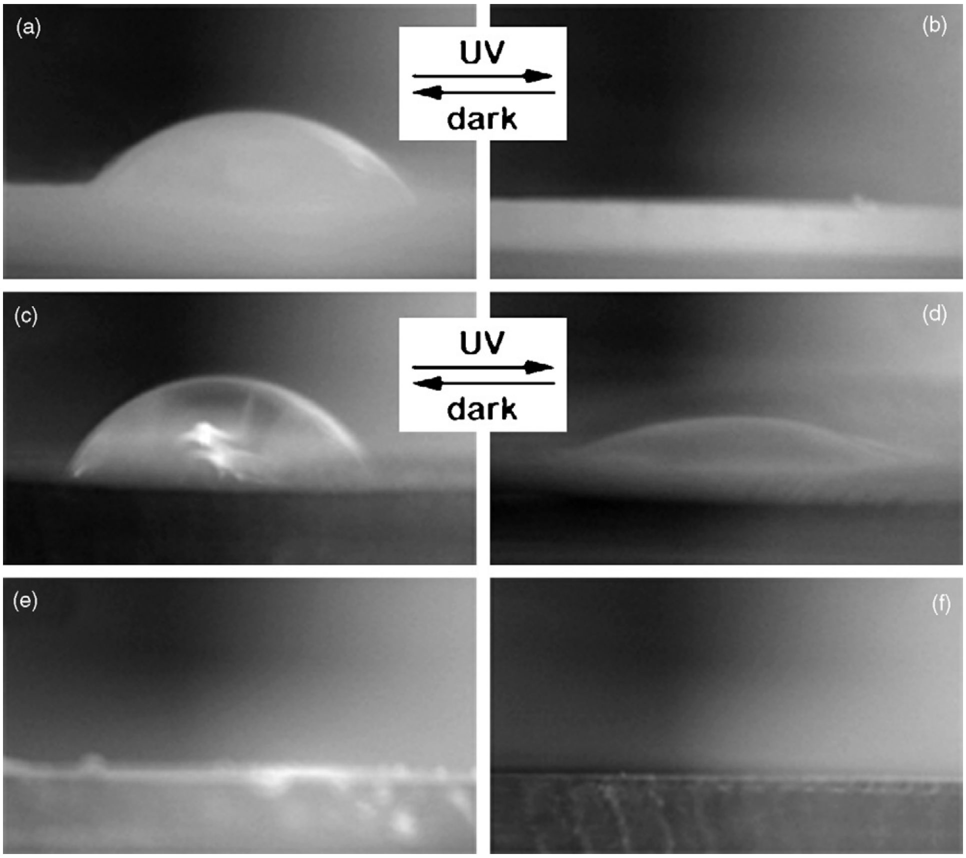

Fig. 3. Water contact angle photographs for the as-deposited and UV-treated ZnO structures: (a and b) 2 h growth on glass before and after illumination, (c and d) 2 h growth on ITO before and after illumination, (e) as-deposited 5 h growth on glass and (f) as-deposited 5 h growth on ITO.

Following the results presented in Figs. 1, 3 and 4, one can see that the deposition of ZnO rods on glass substrates increases its roughness but does not change its initial contact angle, indicating that the deposited structures are less or equally hydrophilic than flat glass. On the other hand the deposition of ZnO rods resulted in a significant reduction of the initial contact angle of the hydrophobic ITO substrate suggesting that these structures are hydrophilic. Moreover, the contact angles always decrease as the surface roughness increases with growth time (as shown in Fig. 1), for both substrates used. Therefore, our results are consistent with the Wenzel's model, since this is the only one predicting a decrease of the contact angle with increasing roughness and the possibility of super-hydrophilicity for very rough surfaces, such as those obtained for more than 5 h growth. As we have already mentioned, samples grown for 5 and 10 h exhibit near-zero contact angles in the as-deposited state. We have observed that water droplets spread even more on these surfaces after prolonged UV illumination indicating enhancement of hydrophilicity. In both cases the near-zero contact angles are under detection limits.

Regarding the light-induced modification of the wettability of the grown ZnO structures, Fig. 3b and d present the wetting angle images after the UV irradiation of the 2 h structures grown on glass and ITO, respectively. The corresponding contact angle measurements versus UV illumination time are presented in Fig. 4. As one can see, only the samples grown for 2 h, on both glass and ITO substrates, exhibit a significant photo-induced change in their wettability. In particular ZnO structures deposited on glass exhibit a remarkable photo-induced transition to super-hydrophilicity, reaching a nearly zero contact angle in short time, the response being less pronounced for the ITO case. The efficiency of these changes is quite remarkable and similar to that observed in ZnO coatings produced by more complicated methods [6]. It should be emphasized that these wettability changes are reversible, since dark storage reconverts the super-hydrophilic surfaces to their original states. On the other hand, as shown in Fig. 4, there is a remarkable difference in the dependence of the water contact angle upon irradiation between the samples grown for 2 h on glass and ITO, respectively. Understanding the kinetics of the contact angle upon irradiation is undoubtedly a highly interesting but demanding task. However, the different mechanisms behind the kinetics of such wettability changes are still a matter of controversy [18], hence further studies are needed to clarify this issue.

As far as it concerns the origin of the photo-induced hydrophilicity, it has been reported [6] that UV irradiation can generate electron-hole pairs in the ZnO surface, some of the holes reacting with lattice oxygen to form surface oxygen vacancies. Meanwhile, water and oxygen may compete to dissociatively adsorb on these vacancies. The defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption. As a result, the surface hydrophilicity is improved, and the water contact angle can significantly be reduced. It has also been demonstrated that the surface becomes energetically unstable after the hydroxyl adsorption. Since the oxygen adsorption is thermodynamically favored, it is more strongly bonded on the defect sites than the hydroxyl group [6]. Therefore, the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms when the UV-irradiated samples are placed in the dark. Subsequently, the surface evolves back to its original state (before any UV irradiation), and the wettability is reconverted. Regarding the ACG samples grown for 1 h, which didn't show any photo-induced change of the contact angle, this is possibly due to their low surface roughness and limited substrate coverage.

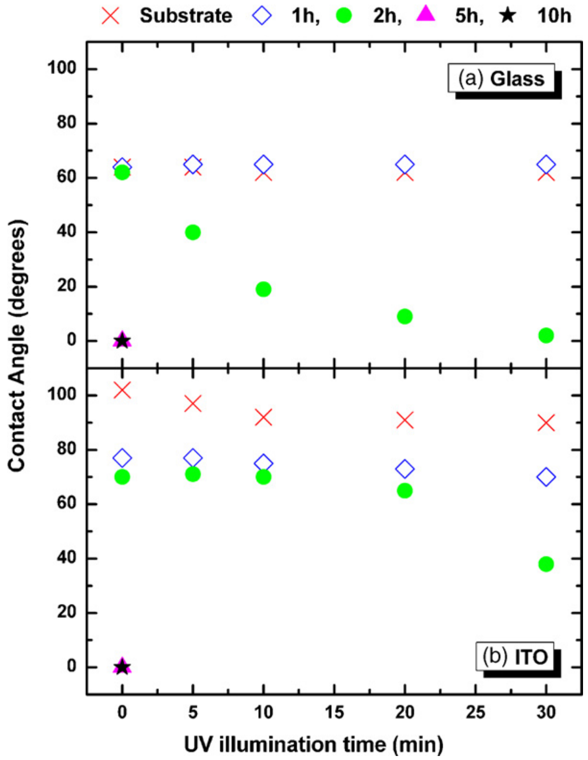

Fig. 4. Variation of the water contact angle of the ZnO structures on glass (a) and ITO (b) substrates as a function of the UV illumination time.

Both properties suggest that the total interface between water and the grown structures is low, leading to a significant reduction of the number of photo-active defect sites, which are in contact with water molecules. On the other hand, it is highly possible that the ZnO particles deposited in these samples do modify their hydrophilic behavior upon UV illumination, leading to a change of the local microscopic contact angles with water. However, such change may not be sufficient to cause a significant reduction of the apparent macroscopic wetting angle, as it is experimentally observed. As a result the UV-induced hydrophilicity is limited. On the basis of this analysis, it can be concluded that the ACG method can yield ZnO surfaces which can exhibit a reversible and efficient change in their wetting properties.

4. Conclusions

Transparent hydrophilic ZnO microstructures with hexagonal wurtzite crystal structure were obtained using the ACG method. As the growth time increases, ZnO rod-like structures transform into flower-like architectures, while the substrate coverage and the macroscopic surface roughness increase. Before irradiation, all samples are intrinsically hydrophilic, with the samples grown for quite long times being super-hydrophilic due to their ultra-high roughness. ZnO structures grown for 2 h were found to exhibit a remarkable reversible transition to super-hydrophilicity after exposure to UV light. We conclude that the ACG method can be employed to control the structural and morphological properties of ZnO structures, resulting in reversible efficient wettability changes. Such capability may be useful for the production of coating suitable for self-cleaning applications.

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