Growth of superhydrophobic Zinc oxide nanowire thin films

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1. Introduction

Zinc oxide is currently one of the most important technological materials that has an almost unrivalled range of applications. Areas of applications range from biomedical, optical, optoelectronics to photo-catalysis, magnetism and terahertz devices [1–5]. The wide variety of applications of ZnO can be attributed to its structure (crystal, band and electronic), large band gap, refractive index, transport properties and the possibility of growing both p and n type forms. In addition, ZnO can also be grown both in the form of bulk crystals and thin films. There has been recent interest in growing ZnO nanowires leading to some new applications such as water repellent surfaces. ZnO nanowires have been grown mainly by chemical methods that may be facile but suffer from the possibility of generating unwanted residual products of the reactants as well as the use of catalysts [1–8]. Furthermore, the compatibility of such methods with processes that involve fabrication of multilayered devices is questionable. Recently, there were reports that the transformation of physical vapour deposited Zn thin films to ZnO by a simple thermal treatment results in the formation of interesting nanostructures [9–11]. Based on this theme, in this work we demonstrate the formation of ZnO nanowires by thermal heating of Zn films deposited onto borosilicate glass and quartz substrates. It is demonstrated that the growth of nanowires does not involve very high temperatures or the use of catalysts. The ZnO nanowire films are shown to be superhydrophobic with water contact angles of the order of 150°. Significantly the superhydrophobic behaviour is reversible under UV irradiation.

2. Experimental details

Zn films were deposited onto borosilicate glass (BSG) and quartz substrates by the thermal evaporation process in high vacuum \((5 \times 10^{-8} \text{ mbar})\). The source substrate distance was 2.5 cm and the substrates maintained at ambient temperature during deposition. Film thickness measured using a surface profilometer (XP 100 of Ambios Technology, USA) was of the order of 500 nm. The as deposited films were post-deposition annealed in air at 200, 400 and 500 °C for 30 min. The morphology of the films was obtained in a Field emission-Scanning electron microscope (Ultra55 of Carl Zeiss, Germany). The X-ray diffraction patterns were recorded in a high resolution diffractometer using Cu Ka radiation of 0.15406 nm (Discover D8 diffractometer of Bruker, Germany). Contact angle measurement was carried out with Rame-Hart contact angle goniometer (model250) equipped with CCD camera. We have used 2 μl droplet of water for contact angle measurement.

3. Results and discussion

The X-ray diffraction patterns of the as deposited Zn film on the BSG substrate and the films annealed to 200, 400 and 500 °C are shown in Fig. 1(a) to (d). It is observed that up to an annealing temperature of 400 °C the films show peaks that can be indexed as belonging to Zn. At 400 °C there is appearance of a weak reflection at a two theta value of 28° that can be indexed as belonging to ZnO which suggests the initiation of oxidation of the films. At 500 °C
there is complete transformation into ZnO as evidenced by the disappearance of peaks belonging to Zn metal film. The observed peaks can be indexed as arising from the hexagonal ZnO structure, with no evidence for unreacted Zn. The behaviour on quartz substrates (not shown here) is the same. This is significantly different from the work of Li et al. [9] and Barshillia et al. [10] who have observed significant residue of elemental Zn even after oxidation of the Zn films at high temperatures. It may be noted that the melting point of Zn is 420 °C. Therefore, at 500 °C the Zn film melts. As the film melts and the Zn – Zn bonds break, the Zn atoms react with the ambient oxygen to form ZnO. Furthermore, since the annealing temperature is much greater than the melting point of elemental Zn, there is sufficient energy for the crystallisation, in addition to the chemical reaction resulting in the formation of ZnO. This can also be inferred from the decrease in crystallite size as a function of annealing temperature. The crystallite sizes calculated using Scherrer’s formula were 120, 98, 67 and 58 nm at ambient, 200, 400 and 500 °C respectively. In addition there was decrease in thickness of the films, at 500 °C, by approximately 10% due to Zn re-evaporation.

Evidence for the melting process is presented in the form of Scanning Electron micrographs shown in Fig. 2(a) to (d) for the as-deposited, 200, 400 and 500 °C annealed films respectively. The as deposited films shows densely packed aligned triangular grains (Fig. 2(a)), which is retained even at an annealing temperature of 200 °C (Fig. 2(b)). At 400 °C the initiation of the melting process is evidenced by the smearing of the grain boundaries and loss of shape of the grains. The grains of the films are no longer separated by well defined boundaries. The transformation in morphology at 500 °C is more remarkable as seen from Fig. 2(d). The grains merged together to form a large “ball-like” mass, which is a clear consequence of the process of melting and flowing. The ball also has several needle-like structures that project outward from the surface. Closer examination of this feature (Fig. 2(e) and (f)) shows that it is comprised entirely of nanowires of 15–100 nm diameter and lengths of the order of 500 nm. It is also seen that the film below this ball is not a continuous film but consists of nanowires. The expanded view of the film (Fig. 2(f)) below the ball confirms that the rest of the film is comprised of nanowires. Thus, the nanowires are formed all over the BSG substrate. The SEM image of the as deposited Zn film on quartz substrate, displayed in Fig. 3(a), shows that the film (as in the case of BSG substrate) are comprised of triangular grains. On annealing these films to 500 °C, as observed from Fig. 3(b), there is transformation in to nanowires of diameters between 50 to 100 nm. Again these nanowires are uniformly spread over the entire substrate.

Fig. 1. X-ray diffraction patterns of the as-deposited Zn film and the films annealed at 200, 400 and 500 °C.

Fig. 2. SEM images of the (a) as deposited Zn films on BSG substrates and annealed to, (b) 200, (c) 400 and (d) 500 °C; (e) and (f) show the expanded view of the films annealed to 500 °C.
surface. The mechanism of formation of nanowires is the process of self-catalysis as proposed by Dang et al. [12] and Zacharias and co-workers [13,14]. In this process, the melting metal plays the role of reactant and catalyst simultaneously, which makes it different from the VLS mechanism of nanowire growth. It may be noted that the nanowires are, in general, aligned, parallel to the surface of the substrate. Thus, the mechanism of the nanowire formation and the alignment appears to be related to the alignment of the triangular Zn grains along the plane of the substrate. Therefore, during the melting process, the reconstruction of the morphology into ZnO nanowires occurs in a direction parallel to the substrate. This is again different from other processes where the nanowires are either vertically or randomly aligned. Although nanowire formation using processes at much lower temperatures such as 95 °C are reported, the current process is very fast as compared to the 4–6 h required in the lower temperature process [8]. An additional advantage is that the initial film is deposited in vacuum ensuring purity of the material.

There are a few reports that ZnO nanowires are superhydrophobic [8,15], hence the wettability behaviour of these nanowires was carried out in the present study. The images of the water droplets on the as deposited and annealed films are presented in Table 1. The contact angle, to water, of the as deposited Zn films on BSG showed a contact angle between 112 to 122° while the Zn films deposited on quartz displayed regions of wetting with contact angles of about 138–142°. The experimental error in measurement of contact angle is ±2°, over about 10 measurements, and the changes beyond this range are attributed to the difference in morphology over the film. On annealing at 500 °C, while Zn films over BSG did not show a significant change in contact angle (116–122°). The contact angle of water on ZnO films over quartz showed three distinct regions of contact angles, reaching values between 150.6–154°. Significantly the films annealed at 500 °C also exhibited a wettability reversal under UV irradiation going from a superhydrophobic (contact angle>150°) to superhydrophilic (contact angle<10°) for exposure of about 1 h, that makes these films particularly suitable for self-cleaning and photocatalytic applications. The differences in contact angles on BSG and quartz are attributed to the differences in roughness of the films on these substrates.

4. Conclusions

The growth of ZnO nanowire films by the annealing of Zn films at 500 °C is demonstrated. The nanowires are horizontally aligned with 15–100 nm in diameter and about 500 nm long. The so formed ZnO films over BSG/quartz annealed at 500 °C are hydrophobic/superhydrophobic and exhibit a wetting transition to superhydrophilic state for UV exposure of 1 h.

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