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To cite this article: C X Xu *et al* 2007 *New J. Phys.* **9** 381

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Optical function of bionic nanostructure of ZnO

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New Journal of Physics **9** (2007) 381

Received 6 August 2007

Published 24 October 2007

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/9/10/381

Abstract. A novel bionic network nanostructure of zinc oxide (ZnO), which is similar to the microstructure of a butterfly wing, was first fabricated by a vapor-phase transport method using zinc powder as a source. These bionic nanostructures are composed of three ordered multi-aperture gratings. Similar to the optical effect of butterfly wings, the diffraction patterns of the bionic network of ZnO were observed. The mechanism of the optical function was discussed based on the physical model of multi-aperture diffraction.

The microstructures of butterfly wings consist of natural photonic crystals and present charming colors due to pigment absorption, diffraction and interferences [1]–[3]. Great efforts have been made to construct artificial photonic crystals using silicon, polystyrenes, etc [4]–[7]. In general, careful design and strict processes are required, such as using complicated laser technology and chemical self-assembly, to obtain the desired structures, especially for three-dimensional (3D) configurations. Simplified fabrication and improved performance of photonic crystals are very useful for future photonic devices.

On the other hand, zinc oxide (ZnO), as an important semiconductor has attracted great interest in recent years because of the large direct bandgap, strong exciton binding energy and applications in optoelectronics and sensing. In this area, considerable attention has been paid to ZnO nanostructures and p-type doping. So far, besides various quasi-1D nanowires, nanorods and nanobelts, abundant 2D and 3D nano-/microstructures with regular configurations, such as nanocombs, nanodisks, hexagrams, nanorings, superlatticed nanohelices and networks, have been fabricated by control of the growth conditions based on the polarity and surface

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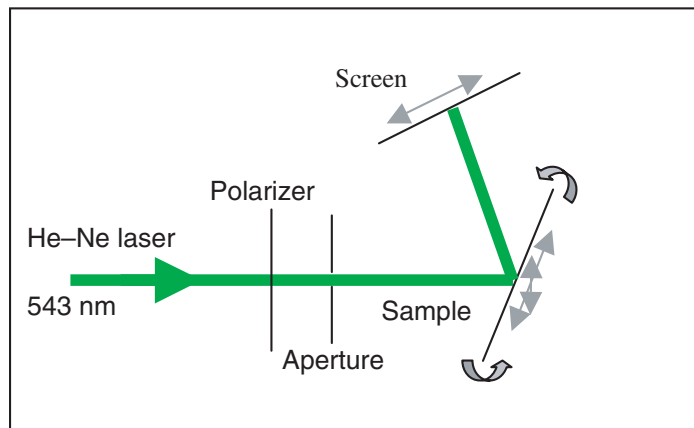


Figure 1. Schematic diagram of the set-up for optical diffraction.

energy of ZnO [8]–[15]. Meanwhile, the characteristics of nanostructural ZnO have also demonstrated versatile applications, such as nanolasers, field emitters, nanotransistors, sub-wavelength waveguides and nanogenerators [8], [16]–[19]. Even so, the rich morphologies of ZnO still inspire many researchers to explore and develop new functions of nanostructural ZnO. In this paper, a simple vapor-phase transport method has been employed to fabricate a bionic 3D network structure which shows similar microstructures and optical effects to a butterfly wing. The results reveal not only a novel morphology but also a novel function of nanostructural ZnO.

The ZnO nanostructure was produced in a tube furnace with two constant temperature zones. High purity Zn powder source material held in a small Al_2O_3 boat was placed into a slender one-end-sealed quartz tube near the closed end. A strip of silicon wafer with (100) plane was put into the quartz tube as substrate. The source temperature was kept at 750 °C, and the growth temperature was kept at about 450 °C. The sample was taken out from the furnace after growth for 30 min in air. The x-ray diffraction pattern (omitted here) demonstrated the product is composed of wurtzite structural ZnO. The morphology of the product was examined by JEOL JSM-5910LV scanning electron microscopy (SEM).

The schematic diagram of the optical experiment set-up is shown in figure 1. A He–Ne green laser at 543 nm with power of 5 mW and a semiconductor blue laser at 473 nm with power 25 mW are employed as light sources for diffraction measurement. The power of the blue laser is stronger than that of the green one. An aperture confines the light beam in a diameter of 2 mm. As indicated in figure 1, by moving the sample in vertical and horizontal directions to a proper spot and rotating it to adjust the incident angle of the laser beam, diffraction patterns could be observed on a white screen and then recorded by a digital camera.

At low magnification, ZnO microballs were observed on the substrate through SEM. Figure 2 shows the top-view SEM images of a representative microball surface with medium and high magnifications. It is interesting to note, from figure 2(a), that the surface of the microball is covered with regular network structures. The enlarged SEM images further reveal that the ridges of the network backbone construct three ordered structures. The first one is the long stems as shown by the highlighted red lines in figure 2(b), which are parallel to each other with a period of about several microns. The second one is a grating-like structure as highlighted in green in figures 2(b) and (c), which grows among the first-ordered structures and parallel to each other

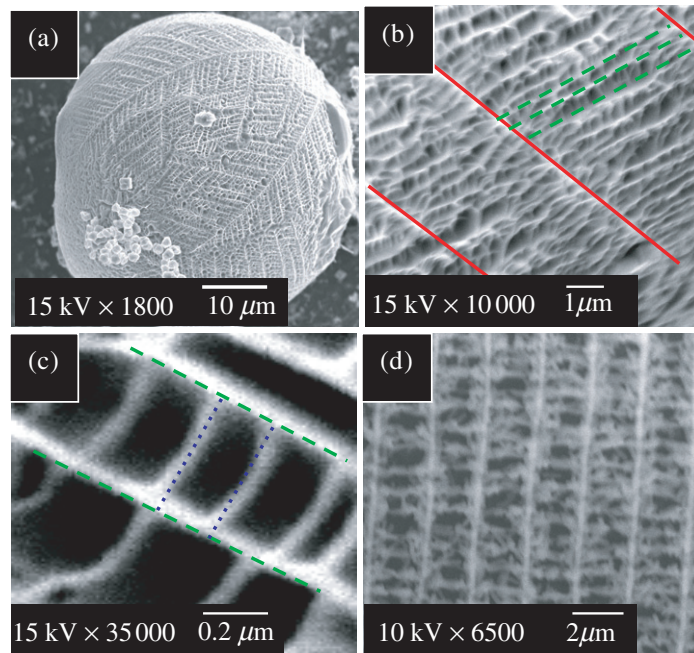


Figure 2. SEM images of the microball surface with medium (a) and high (b) and (c) magnifications and a similar microstructure of a butterfly wing (d). The three-ordered configurations of the ZnO microball are highlighted by the solid line, dash line and dotted line, respectively.

with a spacing of about 400 nm. The third order is also parallel gratings among the second ones with a spacing of about 200 nm. It is worth mentioning that the network morphology of the ZnO nanostructure belongs to a bionic structure. For comparison, figure 2(d) presents a SEM image of a butterfly wing. Similar geometrical shapes of butterfly wings have also been reported previously [1]–[3]. The main long stems and the linked short subordinates are analogous to the second- and third-ordered structures of the ZnO network nanostructures.

The growth mechanism of the bionic nanostructured ZnO is complicated and will be discussed in another paper separately. In this paper, we shall mainly investigate the optical function of the novel nanostructure. It is well known that some butterfly wings are natural photonic crystals and have special color effects caused by absorption, interference or diffraction of their spatial regular structures. The similar bionic structure of ZnO also exhibits some optical effects. By adjusting the incident angle of the irradiated green He–Ne laser at a proper spot, a clear diffraction pattern can be observed on the screen, as shown in figure 3. This phenomenon can be explained through the diffraction model of multi-apertures inserted in figure 3. The intensity of the diffracted light is the overlap of contributions from single-aperture diffraction and inter-aperture interference. When the incident and diffractive angles satisfy the following grating equation, the diffracted light reveals bright patterns.

$$d(\sin \varphi + \sin \theta) = \pm k\lambda, \quad (k = 0, 1, 2, 3, \dots), \quad (1)$$

where d is the space between two adjacent apertures, φ and θ are incident and diffractive angles, respectively and λ is wavelength of the irradiated laser. In a simple case of right incident light

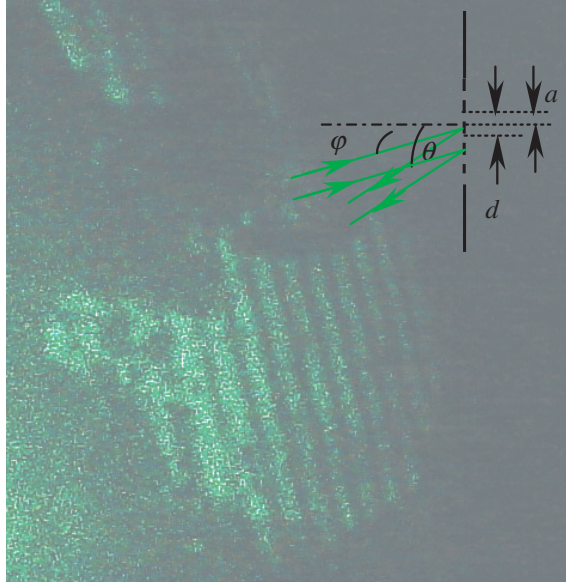


Figure 3. Diffraction pattern of the ZnO bionic nanostructure using a green laser (543 nm) as light source inserted with the schematic diagram of multi-aperture diffraction.

($\varphi = 0$), the intensity of the diffractive signal can be expressed as:

$$I = A^2 \left(\frac{\sin u}{u} \right)^2 \left(\frac{\sin Nv}{v} \right)^2, \quad (2)$$

where $u = (\pi a/\lambda) \sin \theta$ and $v = (\pi d/\lambda) \sin \theta$, a is the width of an aperture, N is the number of apertures covered by the incident light beam and A is the amplitude of the light wave. The terms $(\sin u/u)^2$ and $(\sin Nv/v)^2$ are the single-aperture diffraction factor and inter-aperture interference factor, respectively. In the present ZnO bionic structures, the contribution of the first-ordered structure to diffraction and interference can be ignored because the space between the adjacent structures is about several microns, which is much more than the wavelength of the incident light. The optical pattern in figure 3 should mainly originate from multi-aperture diffraction of the second gratings.

Figure 4 presents a complicated diffraction pattern which was taken from the screen when a stronger blue laser was employed as the light source. The enlarged images in figures 4(b) and (c) show some oblique, bent and crossed diffraction stripes besides the parallel ones. The inhomogeneous patterns should be related to the complicated network structures on the ZnO sphere surface. The diffraction signal should include the contribution from the third-ordered structure. Different from the gracile aperture of the second-ordered structure, the width a and the length b of the third-ordered gratings is only about 200 nm, and the diffraction is generated by the rectangle multi-apertures. Figure 4(d) presents a schematic diagram of the diffraction of a rectangle aperture. In this case, the single-aperture diffraction factor in equation (2) has to be modified by considering the 2D confinement and expressed as $(\sin \beta/\beta)^2(\sin u/u)^2$, where $\beta = (\pi b/\lambda) \sin \theta'$, and $(\sin \beta/\beta)^2$ describes the diffraction item in the length region of a single rectangle aperture in the direction of θ' , as shown in figure 4(d).

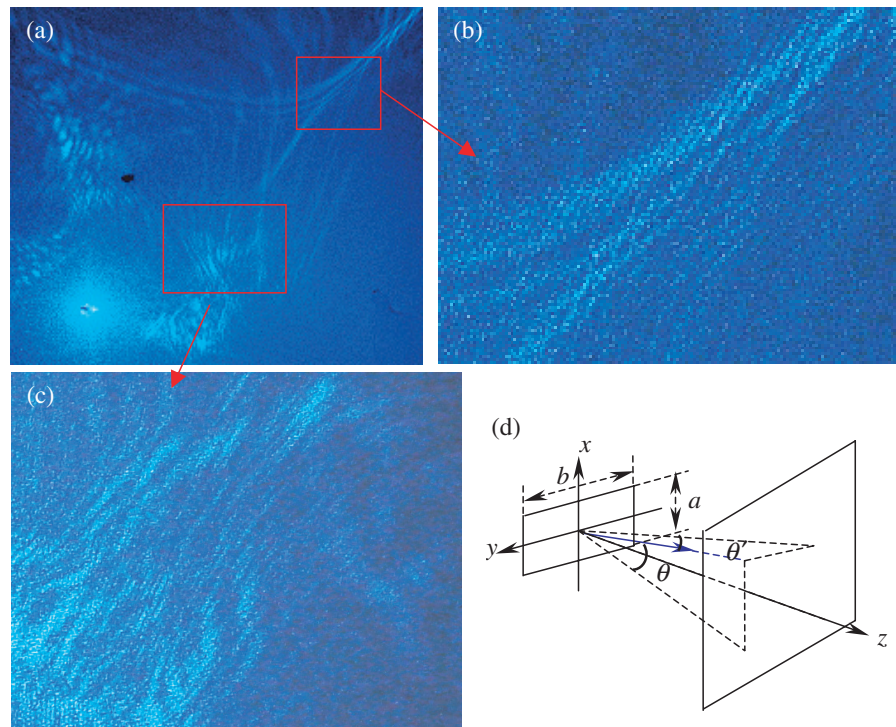


Figure 4. Diffraction patterns of the ZnO bionic nanostructures using a blue semiconductor laser (473 nm) as light source (a) and the enlarged two parts (b) and (c), and the schematic diagram of a rectangle-aperture diffraction (d), where θ and θ' are diffractive angles of the blue diffractive light in xz and yz planes, respectively.

In summary, bionic nanostructures of ZnO were fabricated by the vapor-phase transport method using Zn powder as source. The morphology presents three ordered parallel stripes: the first ones are long stripes with inter-spacing of several microns, the second ones grew among the first orders with inter-spacing of about 400 nm and linked the adjacent first ones, and the third ones are short gratings linking the adjacent second ones and have inter-spacing of about 200 nm. These network structures act as gratings for optical diffraction similar to some butterfly wings. Corresponding to the geometry of the bionic nanostructure, complicated optical diffraction patterns were observed. Based on the physical model of multi-aperture diffraction, the optical effect of the bionic nanostructures was interpreted. The bionic nanostructure cultivated a new member of the ZnO family with abundant aesthetic morphologies and demonstrated a novel function of nanostructured ZnO. It is expected to find application in optoelectronic, photonic areas as novel nanodevices, such as microoptical microelectronic mechanical systems, optic splitters and sensors.

Acknowledgments

This work is supported by NSFC (60725413, 60576008 and 10674023), 863 (2006AA03Z313), 973 program (2007CB936300), RFDP (20050286004) of China and SERC (0421010010) from A*STAR, Singapore. We also appreciate Dr X H Ji for providing the SEM image of a butterfly wing.

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