Low-Temperature Synthesis of *c* Axis Oriented Submicrometer-scale ZnO Cones

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Submicrometer-scale, single crystalline ZnO cones required to function as ultrahigh frequency electroacoustic transducers has been synthesized using LbL chemical route on glass substrate and textured growth along *c* direction perpendicular to surface substrate after annealing film at 200 °C was observed.

ZnO thin films posses the unique properties such as wide direct band gap (3.4 eV) and large exciton binding energy (60 meV) at room temperature, leading to a wide variety of potential applications in catalyst, gas sensors, piezoelectric devices, and solar cells.[1] Huang and co-workers,[2] observed a UV-laser emission at the room temperature using ZnO nanowires. Because of size and quantum confinement effect, considerable interest has been devoted to grow ZnO whiskers, nanowires, and nanobelts in the past decade.[3] Research on the preparation of ZnO has been undertaken to improve performance of zinc oxide varistors.[4] Kim et al.[5] studied nonlinear property of epitaxially grown ZnO giant grains after heat treatment at 1490 °C for 4 h in air. Their electrical properties were also investigated. ZnO thin films in different forms have been prepared by various methods, including anodic alumina template,[6a] vapor–liquid–solid mechanism,[6b] metal–organic vapor-phase epitaxial growth,[6c] and common thermal evaporation method.[6d–g] But the drawback is that they require extreme conditions and expensive equipments. On the other hand, the soft chemical processes provide a mild condition with a low cost and well-controlled method to develop small grain size materials. Many soft solution procedures have been employed to fabricate ZnO materials in nanoform by thermal decomposition[6h] and also spray pyrolysis.[6i] Layer-by-layer (LbL) method has proved to be a simple, more ever versatile technique for the construction of self-assembled films with controlled thickness and composition.[6j] LbL self-assembled method offers extremely easy way to dope film with virtually any element in any proportion by merely adding it in the cationic solution. Unlike vapor deposition method, it does not require high quality target and/or substrates.

In continuation of our research work on ZnO[6k] thin films with controllable morphologies and stimulated by these studies, here we wish to report evolution of a new morphology of films consisting of single crystalline round shaped cones in a submicrometer-scale by applying LbL technique. In the LbL technique, the cation and anion constituents of film material are adsorbed on the substrate one at a time from different precursor solutions. However, very little work has been devoted to the field of epitaxial growth of compound semiconductors (metal oxides) by LbL technique.

The substrate (soda lime glass) was immersed in the first step in the LbL growth of ZnO cones into reaction vessel, which contains aqueous cation precursor 0.1 M $ZnCl_2$ complexed with an aq ammonia solution (7%). The pH of the solution was adjusted to 7.5. At this pH the main species (99%) in the solution is Zn^{2+} as calculated from the stability constants of different zinc species with chloride and hydroxide.[7] The proportion of Zn^{2+} species decreases at higher pH values, and the hydroxo species of zinc become dominant. Addition of ammonia solution in $ZnCl_2$ results into the formation of $Zn(OH)_2$ precipitates but it redissolves in excess ammonia forming tetraamine zinc complex. The immersion time for the cation precursor was 25 s. In second step the substrate was dried. An adsorption and reaction of the anion from deionized water takes place in the third step (20 s), which acts as an anionic precursor solution. It is noted that temperature of anionic precursor solution must be close to 90 °C. We found that high-temperature treatment promoted film adherence. In first stage, the ammonia-complexed zinc ions adsorbed on the substrate surface, And in the reaction step, hydroxide of the anion precursor solution adsorbed onto the surface and reacted with the adsorbed zinc species giving zinc hydroxide. In the present case, ZnO film thickness was 1.51 μm (measured by cross section of SEM image). By annealing at 200 °C in air, films were completely decomposed to ZnO as evidenced by structural studies.

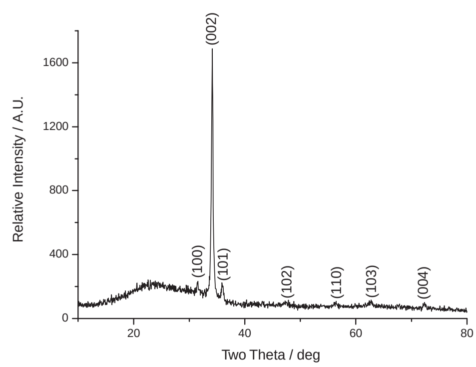

Figure 1. The XRD pattern of ZnO submicrometer cones with preferential *c* axis growth.

The crystal structure and crystallite orientation of the film was examined with a Philips MPD 1880 X-ray powder diffractometer using Cu Kα radiation. Figure 1 show the heat (200 °C, 2 h) treated XRD pattern of ZnO films grown as cones. As confirmed by X-ray diffraction, the films deposited were identified with the Braggs reflections [$a = 3.242$, $c = 5.176$ Å, $P6_3mc$ (180) JCPDS No. 01-1136]. The *c* and *a* axis lattice constants were measured to be 5.20 and 3.21 Å, respectively, consistent with above values for wurtzite structure. Enhanced (002) (2θ of 34.15°) peak intensity indicates the prevailing presence of ZnO submicrometer cones with *c* axis ([001]) normal to the substrate surface. The two other observed reflections at 2θ of 32.8° (100), 35.95° (101) were relatively too small compared with the (002) peak (<10%). Observed an enhanced (002) peak

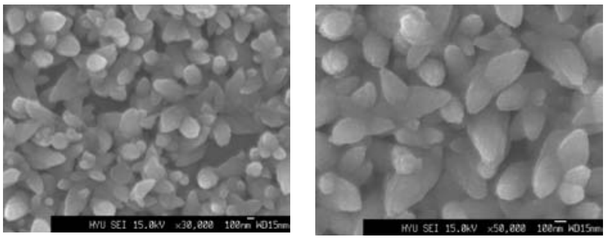

Figure 2. SEM images of submicrometer-scale ZnO cones at two different magnifications.

over the less intense (100) and (101) peaks supports well to the previously reported solution-grown ZnO nanorods.[8] It should be noted that the use of Debye–Scherrer relationship for average grain size measurement in the present case is not valid, since it is a good approximation only for a spherical crystal: the size is universally proportional to the full width at half maximum.[9] Such highly oriented films are required to function as ultrahigh frequency electroacoustic transducers.[10]

Figure 2 shows the scanning electron microscope (SEM) image of ZnO (1.51 μm) film recorded by SM-6340F, JEOL. It seems that nucleation of a solid phase occurred on the some spots of the substrate surface and subsequent crystal growth proceeded radially in the direction of precursor solutions. Figure shows well-defined growth of ZnO cones perpendicular to the substrate surface. It was found in multiple SEM studies that 95% (volume fraction) of the sample was well-defined cones. The energy-dispersive X-ray analysis shows a 1:1 Zn:O composition (not shown) that is consistent with stoichiometric ZnO, revealing that the cones are composed of pure ZnO. A careful look at the image reveals that some of the ZnO cones are perpendicular to the substrate surface and some lean towards the azimuthal direction. Because the angle between the (101) and the (002) plane is approximately 33°, the orientation observed in the XRD diffraction reflects the growth direction of the ZnO cones. Many authors reported different surface morphologies of ZnO under preparative optimized conditions including, nanotubes,[11a] tiny crystals with high density with large specific surface area,[4] giant grains,[5] nanorods,[11b] quantum rods,[7,11c,d] hollow porous structure with wall thickness of 80 to 270 nm and pore diameters of 120 to 600 nm in the form of network,[11e] respectively. Strings like surface morphology with several crystallites aggregated into one grain in hexagonal phase reported through the thermal decomposition process by using four different precursor solutions.[11f] Yin et al.[12a] have fabricated parallel nanorods of ZnO of 2 nm diameter. Zhao and Kwon[12b] reported hydrothermal synthesis of ZnO nonorods. More recently, Hsu et al.[12c] proposed solution-growth method for spatial ZnO nanorods on silver surface using organic templates. As-grown ZnO cones were 0.6–0.8-μm long. Each cone possesses sufficient broad base (0.2–0.3 μm) and narrow top (100 nm). No two cones were mixed (even after crossing) owing to their separate nucleation formation. Each cone is highly crystalline (possibly single crystal) and can be indexed to wurtzite structure identified by XRD (Figure 1). The system was carefully controlled at definite preparative conditions and annealing temperature, respectively, by keeping the substrates vertical.

In summary, an environmentally friendly, safe, cost effective, and reproducible LbL solution system for fabricating ZnO submicrometer-scale cones on glass substrate at low temperature has been successfully developed. ZnO film of 1.51-μm thickness shows effective conical enhancement along *c* axis with separate nucleation formation at preferential regions perpendicular to substrate surface. We are currently perusing the applications of this methodology for various fields including dye sensitization and sensor performance etc.

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