Growth of ZnO Single Crystals by Annealing Sol–Gel-derived Films with PDMS Pre-pressing

Jui-Chi Lee,[1] Ing-Chi Leu,*[2] and Min-Hsiung Hon[1]

[1]*Department of Materials Science and Engineering, National Cheng Kung University, 1, Ta-Hsueh Road, Tainan 701, Taiwan*

[2]*Department of Materials Science and Engineering, National United University, 1, Lien Da, Kung-Ching Li, Miao-Li 360, Taiwan*

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We demonstrate a simple and novel approach for the low-temperature (400 °C) solid-state growth of ZnO micro- and nanorods directly from sol–gel-derived Al-doped ZnO films on silicon substrates without any catalyst. Hot pressing the films by a PDMS pad before annealing has been found to be effective for the creation of ZnO rods. A possible nucleation mechanism of ZnO rods has also been proposed.

Recently, one-dimensional semiconductor materials have attracted increasing attention because of their exceptional properties. Especially, ZnO, a wide band gap (3.37 eV) semiconductor, has potential applications for electro-optics, electronics, and piezo-electrics. ZnO with various morphologies such as nanowires,[1] nanonails,[2] tetrapods,[3] nanoflowers,[4] and tower-like structures[5] has been studied. Various kinds of techniques have also been developed to fabricate single-crystalline ZnO nanorods.[6]

Herein, we describe a simple and novel approach for the low-temperature (400 °C) solid-state growth of ZnO microrods and nanorods by heat treatment of sol–gel-derived films without catalyst. It is interesting to find that the ZnO crystal growth was affected by a contact with the PDMS soft pad before heat treatment. In addition, a moderate amount of aluminum dopant addition may play an important role in promoting the growth of ZnO rods and forming a solid solution as the major support layer in the final stage. This technique may benefit the application of ZnO micro-/nanorods in devices by using relatively low temperatures without metal catalysts.

A heat treatment process for Al-doped ZnO sol–gel films was used for the preparation of ZnO single crystals. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was first dissolved in a mixture of 2-methoxyethanol and monoethanolamine (MEA). The molar ratio of MEA to zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 3 M. The molar ratio of aluminum chloride ($AlCl_3$) in the solution was 0.9 M. The Al-doped ZnO sol–gel films deposition was performed by spin-coating on the silicon substrate. To investigate the effect of film surface conditions on crystal growth, after spin-coating, a flat elastomeric poly(dimethylsiloxane) (PDMS, derived from Sylgard 184, Dow Corning) pad was employed to press the films with different pressures (0.01 and 0.1 MPa were chosen) at 200 °C for 30 min. Then, the PDMS pad was removed from the films. The as-deposited and surface-pressed samples were heat-treated by the same annealing process, i.e., annealed at 400 °C for 3 h in air.

The crystal structure and orientation of the ZnO rods on silicon substrate were examined by XRD at room temperature with Cu Kα radiation. As shown in Figure 1, it can be seen that the peaks can be indexed to a crystalline wurtzite ZnO phase. Only three ZnO(100), (002), and (101) peaks are observed at 31.8, 34.4, and 36.3°, respectively. No other Zn–O compound is observed.

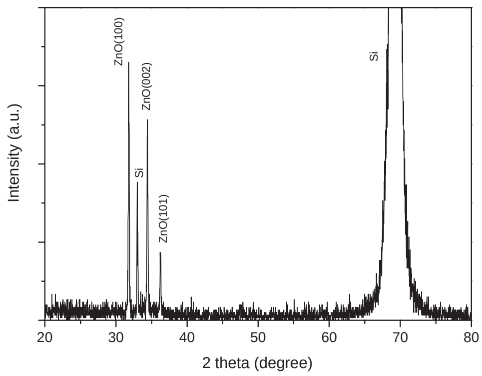

Figure 1. XRD analysis of the ZnO rods.

Typical surface morphology of sol–gel-derived Al-doped ZnO films after heat treatment at 400 °C for 3 h in air is shown in Figure 2. Through the process of stress relaxation, which results from the removal of solvent during the drying period, an isotropic wavy pattern is generated. The pattern formation mechanism has been described elsewhere.[7] In this study, however, the substrate is dramatically covered by ZnO nanorods or microrods instead. Figure 3 shows the SEM images of the ZnO crystals prepared in this study. Nanosized and microsized ZnO rods shown in Figure 3a and Figure 3b, respectively, were fabricated on sol–gel films by annealing at 400 °C for 3 h but with different additional PDMS-pressing of 0.01 and 0.1 MPa pressures, respectively. In Figure 3b it can be seen that ZnO rods are partially embedded in films and grow with random orientations. The SEM images reveal that the average diameters of ZnO nanorods (Figure 3a) are 150–250 nm and the average diameter and length of the ZnO microrods (Figure 3b) prepared at 400 °C are 1 and about 2–3 µm, respectively. The images in Figure 3b show the perfect hexagonal rods with well-developed side surfaces and faceted sharp tips on both ends, which can be attributed to the high crystallinity of the sample. The rods having

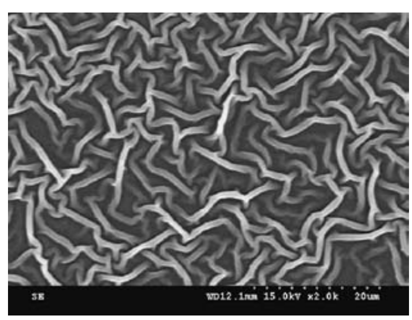

Figure 2. Typical wrinkling morphology of aluminum-doped zinc oxide films after heat treatment. Scale bar is 20 µm.

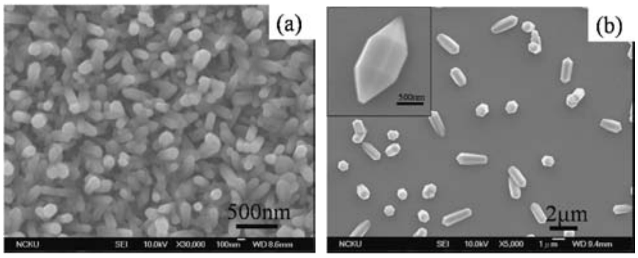

Figure 3. SEM images of ZnO rods with hexagonal pyramid-like tips on both ends by different PDMS pre-applied pressures of (a) 0.01 MPa and (b) 0.1 MPa.

well-developed facets with crystal habits of the ZnO structure also suggest that the rods are single crystals. TEM characterization also confirms their single-crystalline nature (not shown here). In addition, it is found that by controlling the experimental conditions, e.g., sol–gel films surface modification, ZnO rods with different aspect ratios and sizes can be grown by this method.

It is an interesting phenomenon that the final product of this study is much different from the result of a conventional zinc–aluminum oxide sol–gel process. It is well known that various models[8,9] have been proposed to explain the growth mechanism of one-dimensional materials. The vapor–liquid–solid (VLS) mechanism is the most popular one for the growth of 1-D nanomaterials, in which metallic particles as catalyst are usually observed at the ends of the 1-D nanostructures after growth. However, such VLS mechanism does not seem to be applicable to the present system. A possible nucleation and growth mechanism is proposed here. There are two stages for the formation of ZnO rods, nucleation and crystal growth. Since PDMS is permeable to most organic solvents with various degrees of swelling induced in the polymer network,[10,11] it is believed that in the initial stage of the PDMS hot-press process, PDMS pads may absorb some solvent from the sol–gel films and lead conventional wrinkles into segmentation for rod growth. In this study, a lower hot-press pressure results in less deformation of PDMS pads which will absorb more solvent than more deformed ones (under a higher hot-press pressure) and leave less solvent in the films. As the remaining solvent begins to evaporate during the annealing process, rod structure also starts to build up. As a result, thinner films (under lower hot-press pressure) will create a higher density of nuclei growing into smaller ZnO rods. And since no metal catalyst was used for the crystal growth in this study, the nucleation can occur at any site on the substrate. During growth (stage 2), the pressed and still wet sol–gel films may provide liquid source at a lower annealing temperature for nuclei to grow into rods. Under this condition, the nuclei would preferentially grow along opposite *c* axis into rods instead of a wavy network structure. It is also believed that the stress relaxation in this process plays a key role to cause zinc oxide pushing aluminum into the matrix during the crystallization process and create sites for the growth of ZnO nuclei. Zn–O compounds seem to much more easily crystallize and form hexagonal crystal structures than Al–O compounds under doping conditions, while conventional undoped ZnO sol–gel only turns into polycrystalline ceramic structures by the same process.

From TEM analysis, the film matrix contains a huge amount of aluminum and exhibits amorphous structure, so aluminum additives may not only undergo separation from zinc during heating but also form a thin amorphous film supposed to support the nucleation and growth of ZnO crystals and provides a necessary environment for the growth of the ZnO rods[12] at the final stage.

In conclusion, we have fabricated micro- and nanometer scale ZnO rods without using catalyst at a relatively low temperature of 400 °C by a novel simple annealing of sol–gel-derived films on silicon substrate. Hot pressing the films by a PDMS pad before annealing is found to be effective for the creation of ZnO rods. A possible nucleation mechanism of ZnO rods has been proposed. Further investigations may lead to an extension of this technique to the preparation of nanometer scale ZnO nanorods or other nanostructures based on the zinc–aluminum sol–gel films.

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