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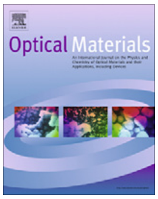

Lateral growth and optical properties of ZnO microcrystal on sapphire substrate

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ABSTRACT

Without catalysis, hexagonal zinc oxide (ZnO) microcrystals were successfully grown on (0001) sapphire substrate in a home made chemical vapor deposition system under atmospheric pressure. A rapid lateral growth at rate of 15 μm/h and a dense growth of ZnO crystals were realized in the growth regions of 800 and 850 °C, respectively. The growth mechanisms were explained similarly with the selective epitaxy. The high quality of the crystals was attested by the X-ray diffraction pattern, Raman scattering and temperature dependent photoluminescence. These results showed the potential of lateral growth ZnO crystals at low cost.

1. Introduction

In recent years, zinc oxide (ZnO) has attracted much attention in the field of optoelectronic applications due to its wide bandgap of 3.37 eV and free exciton binding energy of 60 meV [1,2]. Various ZnO-based devices have also been fabricated, such as ultraviolet (UV) detectors, light emitting diodes (LED), laser diodes (LD), thin film transistors (TFT) and gas sensors [3–7]. However, the performances of these devices need to be enhanced for commerce utilization, which is deeply depends on the crystal's quality. To grow high quality ZnO crystal, the substrate and the growth method should be carefully selected.

In synthesizing ZnO crystal, low lattice mismatched substrates, like GaN, SiC and $ScAlMgO_4$, are favored as they can reduce the strain and the dislocation density [8–10]. However, at present, the growth of large size GaN is a hard work, and the fabrications of SiC and $ScAlMgO_4$ are also expensive and difficult. Therefore, sapphire with a lattice mismatch of 18% is still a usually reported substrate for ZnO epitaxial growth since its considerable size and relatively low cost [11,12]. But, among these reports, the lateral growth of ZnO on sapphire was rarely mentioned, which is an important issue for growing planar ZnO crystal.

On the other hand, the principal methods for synthesizing ZnO crystal are hydrothermal, melting and chemical vapor transport, and a lot of breakthroughs have also been achieved. According to reports [13–16], the best ZnO crystal, 3-in. or even bigger, was grown by the hydrothermal method with Pt lining; 2-in. ZnO crystal was grown by the melting method with PbF_2 as solvent; centimeter scale ZnO crystal was also grown in ampoule by chemical vapor transport using graphite or hydrogen as transport agent. However, the impurity elements, like Li, Na, Pb, C or H from the solvent or transport agent, affected the crystal quality. Moreover, the unusual growth conditions were imperative in these methods, like the autoclave with Pt lining and vacuum sealed ampoules. These needed complex and expensive equipment, led to the costly crystals and limited the progress of ZnO-based devices. Fortunately, among these methods, the chemical vapor method is very flexible for adjusting and refitting into different structures, and may be suitable for growing ZnO crystal at low cost [17].

In this work, a home-made chemical vapor deposition (CVD) system was tried to grow ZnO crystal on sapphire under atmospheric pressure. Without vacuum or high pressure requirements, the composition and operation of the system are simple and safe, and the cost is low. Particularly, the stable concentration of precursor is maintained by mass flow controller, which was hardly realized via direct evaporation of zinc granules. With the optimized parameters, hexagonal ZnO crystals were effectively grown on sapphire without any catalysis. A rapid lateral growth mode was confirmed by the expanding shapes of the ZnO crystals. The nucleation density was also increased by moving the substrate to a low temperature region. The growth mechanisms were discussed, and the crystal quality was evaluated by Raman scattering and photoluminescence (PL). These results hint at the possibility of growing high quality ZnO crystal at low cost.

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2. Experimental details

2.1. CVD system and growth processes

Under atmospheric pressure, the ZnO crystals were grown directly on (0 0 0 1) sapphire in the CVD system which mainly consists of a horizontal resistance-heated furnace, a long quartz tube and two mass flow controllers. The ZnO powder and the gases were of 5 N purity. The main chemical processes of the experiments were HCl reacted with ZnO powder to form $ZnCl_2$ and H_2O, and the reverse reaction occurred in growth region to form ZnO crystals.

Prior to growth, the substrate (10×10 mm^2) was dipped in diluted hydrochloric acid (HCl) and cleaned ultrasonically for 30 and 15 min respectively, and then dried with high purity nitrogen. The lateral growth and the dense growth were performed in two regions of 850 and 800 °C, respectively. For the lateral growth, the substrate was placed in the center of the furnace and 50 g ZnO powder was loaded 5 cm upstream from the center. When the furnace temperature increased to 850 °C, the HCl gas was introduced into the system by a 20 sccm argon flow which was bubbling through HCl acid. A 300 sccm oxygen flow was also introduced to provide an oxygen rich environment. The growth lasted for 1 h under atmospheric pressure, and then the CVD system was air-cooled to room temperature (RT). To ascertain the lateral growth mode, the substrate was reloaded in the center of the furnace and regrown twice in the same condition. For the dense growth, the sapphire was placed 20 cm downstream from the center (800 °C), and the processes were carried out exactly as the lateral growth except for the regrowth. The details of the experiments had been reported previously [18].

2.2. Characterization of ZnO crystals on sapphire

The morphology, crystal structure, vibration modes, and optical properties of the crystals were evaluated by polarizing microscopy (D-35578 Wetzlar, Germany), scanning electron microscope (SEM S-4800, 15 kV), X-ray diffraction (XRD Advanced D8, Germany), Raman scattering, and PL spectroscopy, respectively. The Raman and PL spectra were measured using a JY LabRAM HR800 confocal micro-Raman spectrometer with a multichannel charge-coupled detector. The light source was a 325 nm He–Cd laser. A 40× NUV microscope objective was used for focusing the laser beam and collecting the scattered light. The scattered light was analyzed with a Dilor XY triple spectrometer and a liquid-nitrogen-cooled CCD multichannel detector. The accuracy was better than 1 cm^{-1}. In order to measure the temperature dependent PL spectra, a Helix CTI cycle refrigerator was used for tuning the temperature from 10 to 300 K.

3. Results and discussion

3.1. Morphology and mechanism of lateral growing ZnO crystals

The morphology of the ZnO crystals after lateral growth was observed by optical microscopy, shown in Fig. 1. On the whole substrate, there are just a few crystallites without obvious difference. A typical crystal with average diameter was chosen for observation. Fig. 1a (after the first growth) shows the clear-cut hexagonal crystal with a flat top facet. The second and third growths are shown in Fig. 1b and c, respectively. It is clearly seen that the size of the ZnO crystal is enlarged every time and the hexagonal shape is maintained without significantly changing. However, the three diameters are not exactly equal to each other in every picture and the reason is probably the unsymmetrical distribution of strain in the heteroepitaxy ZnO layer. In the three growths, the average diameters are 41, 80 and 109 μm, which means that the lateral growth rates are about 21, 20, and 15 μm/h. Whereas the three thicknesses of the crystal are approximately 25, 31 and 39 μm, which means that the vertical growth rates are 25, 6, and 8 μm/h. Compared with the first growth, the growth rates along lateral and vertical directions are decreased in the later growths. This is probably due to the increased size of the crystal needing more deposition on its walls. The abnormal vertical rate of 8 μm/h may relate to the measure error from the disuniform surface in Fig. 1c. The final lateral rate is faster than the vertical rate which indicates that the lateral growth of ZnO microcrystal was realized in our home made CVD system.

The SEM images in Fig. 2 show the particular morphology of ZnO crystals after the lateral growth. In Fig. 2a, the hexagonal figuration of the isolated crystal is clearly seen and no smaller crystallite or nucleus around it. Fig. 2b shows the higher magnification surface morphology ranging from the center to the edge of the crystal. In the center, a fluctuant surface with radiate ridges is presented, which may be arose from the dislocations during the heteroepitaxy growth. While near the edge, the fluctuation is decreased and the ridges turn smaller. These are the patterned stains in Fig. 1, and have been grown larger during the regrowth processes. In Fig. 2c, the high magnification surface does not include obvious *c*-axis directional tip which also indicates the comparatively low vertical growth rate of ZnO crystal.

The lateral growth of the ZnO crystal can be explained similarly with the selective epitaxy which was widely used for the growth of InP, GaAs and GaN [19,20]. However, in our experiments, the mask is not the patterned layer but the very few abnormal sites on the sapphire surface, like the ends of the occasional dislocations and other defects. The nucleation occurred on these favorable sites. This supposition is corresponding to the fewness and

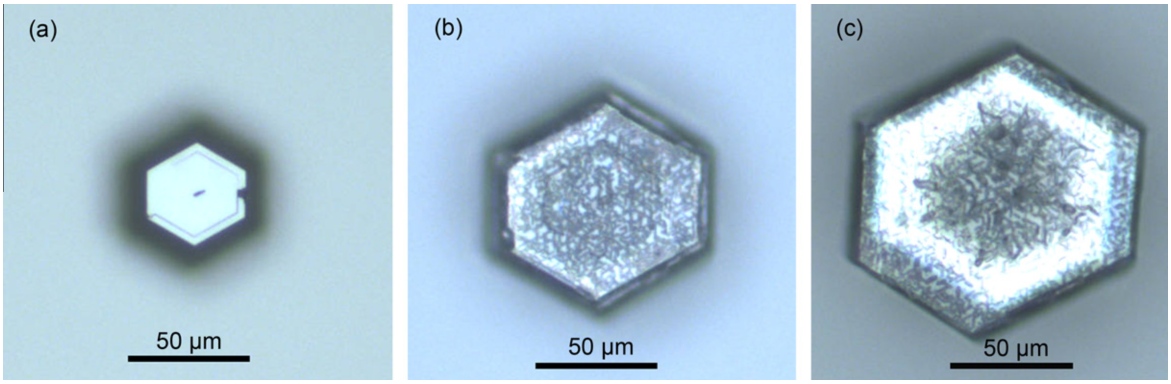

Fig. 1. Morphology of ZnO single crystal in the lateral growth: (a) is the first time growth; (b) is the second time growth; (c) is the third time growth.