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Hydrothermal synthesis of improved ZnO crystals for epitaxial growth of GaN thin films

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Abstract ZnO single crystals with thickness up to 12 mm, 2 inches in "diameter" and weight of about 150 g have been grown from KOH, NaOH, and K_2CO_3 based hydrothermal solutions on the seeds of (0001) orientation. The addition of LiOH up to 3.0–4.5 mol/L allowed to decrease the growth rate of ZnO crystals along the ⟨0001⟩ crystallographic direction. For positive and negative monohedra, it was achieved 0.12 and 0.01 mm/day, respectively, at temperature 340 °C and $\Delta T = 10$ °C. The best ZnO etching agent was found to be the solutions 25 mol% HCl + 3 mol% NH_4F at room temperature, and etching time 5 min. The dislocation density of ZnO crystals varied from 240 cm^{-2} to 3,200 cm^{-2} in the case of growth rates 0.04 mm/day to 0.11 mm/day, respectively. It was also found that ZnO crystals grown are stable in air, oxygen, nitrogen, and argon atmosphere as well as in vacuum at the temperatures up to 1,000 °C under thermal treatment during 4 h.

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Introduction

Zincite (ZnO) has received renewed interest due to its unique combination of physical properties. It has potential applications as improved varistors, transparent high power electronics, optical waveguides, piezoelectric converters, gas-sensing analyzers, window material for display and solar cell, among other application areas [1]. As a direct wide band-gap semiconductor (3.37 eV), ZnO is also a candidate material for emitter devices in the blue to near UV region. Bulk single crystal ZnO, which can serve a device material or as substrates for subsequent epitaxial growth have been grown by a number of techniques: from melt [2], by chemical vapor transport [3, 4] and under hydrothermal conditions [5–8].

ZnO single crystals are particularly promising as a substrate material for heteroepitaxy of GaN based active devices due to their lattice mismatch of approximately 2.6%. In the ZnO structure, oxygen atoms form hexagonal pack, zinc fills a half of tetrahedrons of one orientation, i.e., Zn and O layers are consecutively stacked along the *c* direction. Thus, ZnO single crystals have two polar surfaces: (0001) surface is composed of Zn atoms, but $(000\bar{1})$ surface is an O-terminated face. It is therefore expected that the GaN films grown epitaxially on ZnO substrates

should have the same polarity [9]. Because of both materials are reasonably polar, electrostatic considerations indicate that N- and Ga-faces of GaN should grow on O- and Zn-faces of ZnO, respectively. The polarity of a substrate can be estimated quite easily and unambiguously by measuring the sign of the piezoelectric coefficient.

The use of ZnO as a substrate is complicated by the decomposition of ZnO at high temperatures in reducing atmospheres. For this reason, GaN thin film growth by MOVPE and similar techniques may often be done under sub-optimum conditions. Vacuum-based growth by MBE seems to be more promising. The difficulty of chemically preparing both Zn- and O-face surfaces has lead previous growth studies on ZnO to focus on a single type of substrate polarity. As noted in a 1996 study [9], researchers have concluded that studies of growth on ZnO have further been limited by the difficulty of growing substrate-quality single crystals.

More recent research into the development of a ZnO hydrothermal crystal growth technology utilizing inserts made of a non-noble metal has been successfully carried out by the authors of Refs. [6, 10–13]. These results clearly indicate that further commercialization of large ZnO single crystal is possible for future wide band-gap device applications as well as substrate materials for GaN epitaxial growth. At this stage of development, however, these hydrothermal crystals have a dislocation density of $\sim 10^4\ \mathrm{cm}^{-2}$ with continued improvements expected.

More recently, high quality GaN epilayers have been grown on oxygen and zinc surfaces of ZnO (0001) substrates by MBE, and the effect of the intermediate buffer layer on the structural and optical properties of the GaN films was investigated [14]. X-ray measurements, as well as polarized optical data, confirm that the GaN (0001) planes are parallel to the ZnO (0001) crystal face. The cracks observed in GaN epitaxial layers often noted for growth on both SiC and sapphire are not likely to occur in the case of ZnO substrates. Investigation of the effect of the surface polarity indicates that the best quality GaN epilayers can be obtained using the oxygen face of ZnO as the growth surface. A low temperature, thin buffer layer of GaN or InGaN leads to better optical quality and smoother surface of GaN layers grown on ZnO substrates.

ZnO does therefore show great promise over other types of substrates for this application. Unlike AlN and SiC, ZnO can be grown to large diameter using solution-based growth techniques, which are inherently scalable. This technique is analogous to the commercial production of quartz in which large batch reactors can produce kilograms of single crystals in a single growth run and underpins this critical industry. The development of this growth technology for ZnO bulk single crystals is in progress now in many laboratories. For instance, the authors of Ref. [15] have grown ZnO crystals from hydrothermal solutions. In this case, autoclaves made of high strength steel were lined with platinum inserts to isolate the crystal growth environment from the walls of the autoclave. The crystal quality was high, but the size of crystal grown is not indicated. Recently, the hydrothermal method combined with a platinum inner container was applied to grow large transparent ZnO single crystals with high-purity [8].

In this work, a reliable technology for ZnO crystal growth using corrosion proof non-noble metallic vessels is considered, and the thermal stability and dislocation density of grown single crystals is presented.

Experimental

Steel autoclaves lined with corrosion proof non-noble metallic vessels of 5-l capacity were used for the hydrothermal growth of zincite crystals. Long-term ZnO crystal growth cycles (up to 80 days) were based on the 3.0–4.5 M solutions of KOH, NaOH, K_2CO_3 or their mixtures. Lithium hydroxide LiOH was added for decreasing the growth rates along [0001] direction. All reagents are of 99.98%. Since this complex system has the narrow metastability field, additional studies of composition and concentration of hydrothermal solutions were undertaken, in order to avoid spontaneous nucleation. It was achieved by careful control over the solution composition and density, heating rate of the autoclave during the crystallization process, and maintaining stability over all crystal growth parameters.

The starting ZnO powder was pressed and sintered at 900 °C under pressure 500 kPa. Then, the tablets were loaded in the lower part of the lining vessel (dissolution zone). Plate-like seeds 2-in-size (2 inches in "diameter") prepared from zincite crystals, derived from previous hydrothermal growth runs, and were oriented parallel to (0001) and $(10\bar{1}0)$ were fixed in an upper section of the liner (crystallization zone). Saturated solutions were transferred from the lower more highly heated zone into the higher and cooler zone due to the thermal convection. As a result of supersaturating solution in the upper section of autoclave, lead to deposition of ZnO on the existing seed crystals.

Thermocouples were clamped in the special pockets and placed between the outer surface of insert and internal wall of autoclave. The synthesis was performed under the direct temperature gradient. The temperature in dissolution zone was held at 330–360 °C. The inner pressure varied within the range of 20–40 MPa.

Thermal stability of the grown ZnO crystals was investigated in air, oxygen, nitrogen, and argon atmosphere as well as in vacuum at the temperatures 700, 800, 900,

1,000, 1,050, and 1,100 °C. The morphology, at the micron scale, of ZnO single crystals was observed by optical and electron microscopes before and after each annealing procedure.

Aqueous solutions with different concentrations of HCl, H_3PO_4, oxalic, acetic, ascorbic acids, and NH_4F were tested for selective etching of seed plates, as-grown (0001) faces and slices parallel to c-plane face. Etching time was varied from 5 to 20 min in the temperature range of 20–60 °C.

In order to decrease dislocation density of ZnO crystals, so called "turning" seeds were prepared in two stages. Since dislocations are spread perpendicular to the crystallization front, monohedron slices cut from the grown crystals on the prismatic seed should contain a small number of these defects intersecting the prism surface. At the first stage, $(10\bar{1}0)$-oriented plates were used for ZnO crystal growth. Then, parallel plate (0001) slices were cut from the crystal grown and chemically polished in 9 M NaOH solution.

Results and discussion

Transparent and light yellow-green ZnO crystals with size up to $30 \times 30 \times 12$ mm^3 and weight of about 150 g were obtained in growth experiments (Fig. 1). Zincite crystals grown on monohedral seeds have quite developed two monohedron faces (0001) and $(000\bar{1})$ as well as positive hexagonal pyramid $(10\bar{1}1)$ (Fig. 2). As mentioned above, c axis is polar in ZnO crystal structure. The opposite sides of the seed have different atomic arrangement at their surfaces and, consequently, different growth rates. The growth rate on the (0001) face was up to 0.12 mm/day at 340 °C, but the $(000\bar{1})$ face did not practically grow.

Growth pyramid of positive monohedron is characterized by better quality and larger sizes and it seems to be very convenient for cutting crystal on the later stages of substrate processing. On the whole, monohedral (0001) plane is rather smooth. Although, large single polygonized growth hillocks were observed on its surface.

It is well known that the quality of grown crystals greatly depends on the quantity and type of defects in seeds. On the other hand, some defects such as small cracks and channels in the initial slice may disappear during the growth process. Deflection of seed plane from the monohedral surface not more than 30′ causes the formation of the regeneration zone approximately 0.1–1.0 mm thick with numerous gas–liquid inclusions. Sometimes, appearance of such inclusions results from unstable growth conditions, for instance, seals failure or capture of mechanically generated iron impurities ($\sim 0.6 \times 10^{-4}$ ppm [13]). The twins coming on the surface of a positive

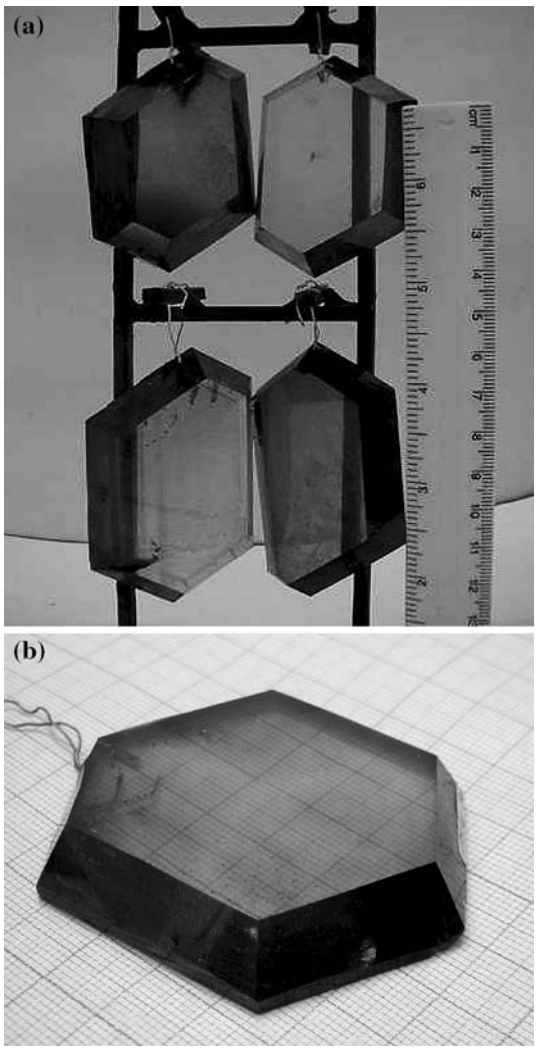

Fig. 1 ZnO crystals grown by the hydrothermal method: (**a**) situated on the frame (portion of the frame shown), (**b**) zinc oxide single crystal

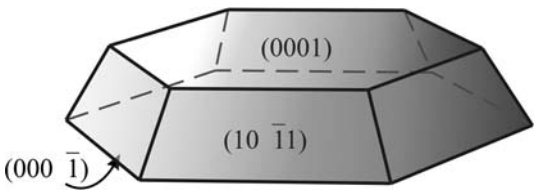

Fig. 2 Schematic drawing of ZnO crystal monohedron indicating principal facets and orientations

monohedron of the seed always wedge out due to difference in growth rates in $[+c]$ and $[-c]$ directions.

In general, the slowest growth rate leads to better crystals because there is a time for the atoms to migrate or diffuse along the crystal surface to the lowest energy sites which are the most stable and lead to a crystallographically regular lattice.

Thermal treatment in air, oxygen, nitrogen, or argon atmosphere as well as in vacuum at the temperatures 700, 800, 900, 1,000, 1,050, and 1,100 °C indicates that these hydrothermally grown zincite crystals are stable at the temperatures up to 1,000 °C for at least 4 h.

In selective etching, sharp-cornered etching pits were observed on the monohedral face. The pattern and density of the etch pits depend greatly on the nature and concentration of chemical reagent as well as on temperature and etching duration. Organic etchants promote indistinct patterns of the etch pits. Inorganic acids characterize by a high preferential etching at defects; however, the etching pits have conic section with round base. In the case of NH_4F, there are small sharp-cornered etching pits with deep etching canals appearing at the bottom of the pits.

The aqueous solutions of 25-mol% HCl + 3-mol% NH_4F seem to be the best for selective dislocation etching of ZnO crystals and possess to reveal linear structural delineations. In this case etch figures were represented by sharp-cornered polygonized pits up to 0.07 mm in diameter cut by faces of negative hexagonal pyramid of high indexes $(10\bar{1}L)$ (Fig. 3). Pyramidal pits were naturally oriented along the crystallographic directions.

Two different kinds of etch pits were observed on the (0001) face of ZnO crystals after defect-selective etching: flat-bottomed and sharp-cornered forms. The first ones were confined to surface defects. Sharp-cornered figures resulted from structural boundaries. Generally, they were isolated (Fig. 3) or formed network structures consisting irregular lines (Fig. 4), attributed to the channels generated at the twin locations or resulting from unstable growth conditions. Network structures consisting of irregular lines were found both in seed slices and layered crystal sections. Optical inhomogeneity was observed in such regions in polarized light.

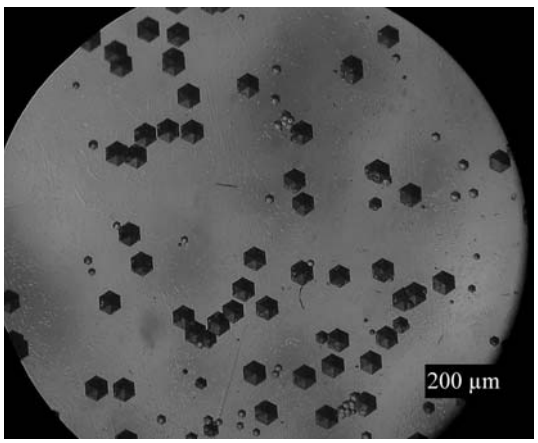

Fig. 3 Sharp-cornered polygonized pits formed using a selective etchant composed of HCl + NH_4F etchant at T = 20 °C and etched for 5 min

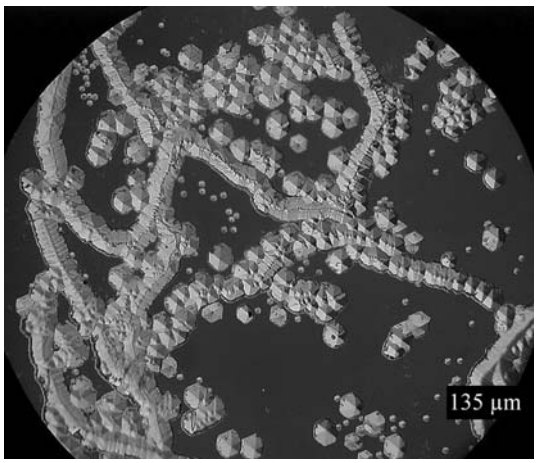

Fig. 4 Network structures consisting of irregular lines formed by etching pits attributed to sub-grain boundaries (monohedron face, HCl + NH_4F etchant, T = 20 °C, 5 min)

The density of single sharp-cornered etching pits varies from n up to $n \times 10^3$ in different crystals (Table 1). High supersaturations of hydrothermal solutions result in increasing dislocation density of the grown crystals. A steep temperature gradient over the crystallization zone leads to significant spontaneous nucleation and formation of twins on ZnO pyramidal faces.

It was found that dislocation density in seeds is much higher in comparison with the layers grown when

Table 1 Experimental results of ZnO defect-selective etching

Sample	Etch pits density (cm^{-2})	Growth rate of the (0001) face (mm/day)
Seed	920	0.11
(0001) slice	3200	
As-grown (0001) face	3200	
Seed	900	0.08
(0001) slice	1300	
Seed	8000	0.10
(0001) slice	5000	
As-grown (0001) face	4000	
Seed	2300	0.07
(0001) slice	560	
As-grown (0001) face	240	
Seed	250	0.04
(0001) slice	250	
As-grown (0001) face	400	
Seed	1400	0.04
As-grown (0001) face	3500	
Seed	3	0.05
(0001) slice	300	

thermobaric parameters were provided by an automatic maintenance of crystallization process. It makes to be possible to grow high quality crystals using seeds that possess rather high dislocation densities (Fig. 5).

Since dislocations are spread perpendicular to the crystallization front, monohedral slices cut from the crystals grown on the prismatic seed should contain a small number of these defects. Selective etching confirms, if

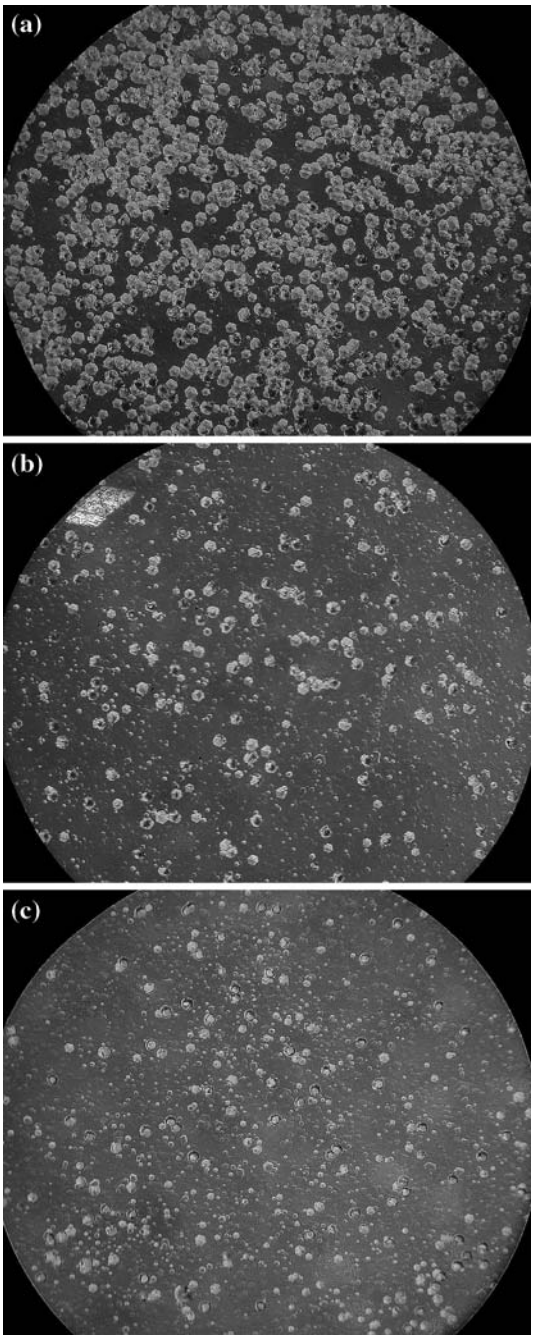

Fig. 5 Etching patterns (×50): (**a**) seed (0001) plate, (**b**) (0001) slice, (**c**) as-grown (0001) face (HCl + NH_4F etchant, T = 20 °C, 5 min)

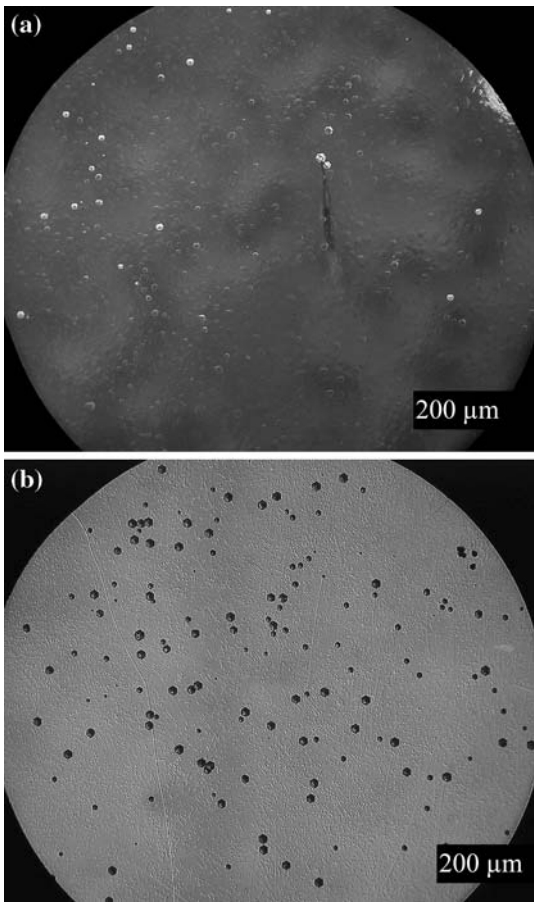

Fig. 6 Etching pattern on the "turning" (0001) seed slice (**a**) and as-grown (0001) crystal face (**b**) after etching in HCl + NH_4F etchant at T = 60 °C for 10 min

"turning" seeds have single etching pits, their number increases during the growth experiment (Fig. 6). Figure 7 shows etching pattern on the as-grown (0001) face of a ZnO crystal obtained on "turning" seed. Defects located in the center of this crystal were inherited from the seed, while they are practically absent at its periphery. Growth rate of the positive monohedron on the "turning" seeds is two times lower than in ordinary crystals. It may be connected with difficulties to initiate a new tangential layer on the growing surface.

Conclusions

A reliable crystal growth technology was developed based on ZnO hydrothermal synthesis. Transparent, light yellow-green color zincite single crystals with size up to 2 inches were obtained. A method of defect-selective etching is suggested to study the underlying microstructure of ZnO crystals. It was found that aqueous solutions of 25 mol% HCl + 3 mol% NH_4F seem to be the best media for defect-

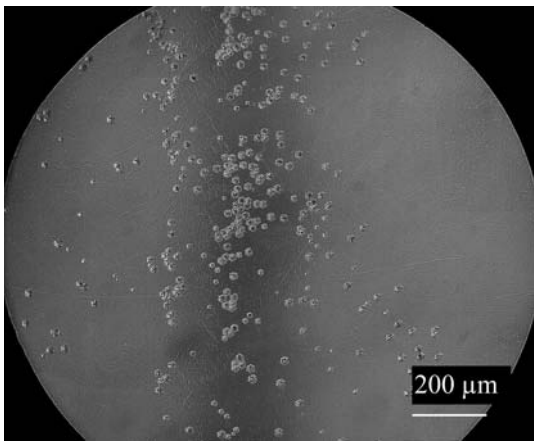

Fig. 7 Etching patterns on the as-grown (0001) face obtained on the "turning" seed (HCl + NH_4F etchant, T = 20 °C, 5 min)

selective etching and can reveal the linear structural boundaries within the crystal. Further investigations revealed two kind of etch pits, which correspond to two different types of defects. Dislocation density depends on the defect quantity in seed slices as well as on growth conditions. High supersaturation, solid inclusions, and temperature fluctuations lead to an increase in number of structural defects. It was shown that usage of "turning" seed slices can be used to grow ZnO single crystal with low dislocation density. It was also found that ZnO crystals grown are stable in air, oxygen, nitrogen, and argon atmosphere as well as in vacuum at the temperatures up to 1,000 °C under thermal treatment up to 4 h. Preparation and examination of ZnO substrates for GaN thin film growth are in progress.

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