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ZnO single crystals: Synthesis and characterization

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Abstract

Zinc oxide crystals grown in a single basic mineralizer in hydrothermal autoclaves are of poor quality. The crystals are transparent, pale green or pale yellow in color depending on different technical growth conditions. The quality of crystals under different conditions was observed by X-ray rocking curves measurement. The use of ultra-pure nutrient improves their perfection and purity. Zinc oxide bulks that were grown by the hydrothermal method in a mixture of KOH and LiOH aqueous solutions are of good quality.

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1. Introduction

ZnO is a wide band gap semiconductor, which has been extensively studied for many years. The main applications of this material were initially related to its high luminescent efficiency and non-ohmic properties [1]. Some early studies showed the applicability of ZnO to the fabrication of laser diodes and light emitting diodes in UV-blue region. Recently, new applications of ZnO on optoelectronics have been developed. The advance in the fabrication of p-type ZnO [2] make it possible to fabricate good-quality optoelectronic devices based on this semiconductor.

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ZnO is recommended as an attractive alternative to both sapphire and SiC as substrates for GaN growth. When growing GaN on (0 0 0 1) sapphire substrates, one has to cope with a 16% lattice mismatch. SiC is better suited as a substrate material, but it is costly and also generates stacking mismatch boundaries in device structures, which shorten the lifetime of the device. For ZnO the lattice mismatch is only 2.2% for GaN and zero for $In_{0.22}Ga_{0.78}N$ [3]. ZnO crystals present several advantages: lattice-matched substrates, high excitation binding energy (60 meV for ZnO versus 20–25 meV for GaN) enabling optical lasing at room temperature and processing feasibility [4]. Many studies on the point defect structure have been conducted, mostly devoted to specify the role of point defects and impurities such as copper in the non-ohmic behavior of ZnO [5]. High quality ZnO single crystals benefit the development of blue and UV emitting devices, and are also a prosperous substrate material for the subsequent epitaxial growth of other semiconductors.

The important point is how to grow high quality ZnO single crystals under different technical conditions. Demianets et al. [6] analyzed the polar growth and non-stoichometry of ZnO crystals in terms of crystal chemistry with duo to regard for physicochenemical conditions of the growth mediums. Sekiguchi et al. [7] studied the optical property of sectors of ZnO crystals by cathodoluminescence. While they did not use the rocking curves to illustrate the crystal quality, neither did they compare the results of obtained crystals under different growth conditions. The experiments and analysis of the influence of crystal growth factors are put forward and discussed in this paper.

2. Experimental procedure

The autoclaves used for the growth of zinc oxide crystals were of similar design to those used for the preparation of synthetic quartz with a bore of 50 mm and internal length 600 mm except for precious metal liner. Initially commercial 99% zinc oxide powder was used as the nutrient material but this was later replaced by ultra-pure 99.99% zinc oxide powder that we prepared at lab. A tighter control was applied on the particle size of ultra-pure ZnO powder to ensure that the sintered pellets remained intact during the growth process. The powder was pressed into pellets, which were sintered at 1350 °C, then cracked to obtain the granule size of 1–6 mm. The lithium hydroxide, sodium hydroxide and potassium hydroxide used as solvents were specially prepared, which were of reagent purity. The seeds were vapor grown and plane-parallel plates cut from hydrothermally grown bulk ZnO single crystals normal to the given crystallographic directions. Prior to experiments, the seed plates were etched in HCl and NaOH solutions subsequently to remove the layers distorted during sawing the samples. The temperature in the growth zone ranged within 300–400 °C. The temperature gradient between the growth and dissolution zones (along the external wall of the autoclave) ranged within 10–15 °C. The inner pressure varied within 100–150 MPa. A convenient baffle construction was 5–6% open with one-half of the space in a central opening and the remaining distributed about the periphery. Chemical analysis of the crystals was performed by inductively coupled plasma (ICP) to estimate Li, K, Na and Fe. The quality of the grown ZnO single crystals was characterized by X-ray diffraction (XRD) scans using Cu Kα radiation monochromatized by four crystals of Ge (2 2 0).

3. Results and discussion

Because of its very high melting point of 1900 °C and of its high reactivity with any surrounding material but platinum [8], cm-sized ZnO crystals are difficult to be grown from the melt, and are difficult

Table 1
Growth conditions of grown crystals

Run	#1	#2	#3	#4	#5	#6
Nutrient powder	Commercial	Ultra-pure	Ultra-pure	Ultra-pure	Ultra-pure	Ultra-pure
Solvent	KOH 5 m + LiOH 1 m	KOH 5 m + LiOH 1 m	KOH 5 m	NaOH 5 m + LiOH 1 m	KOH 5 m + LiOH 1 m	KOH 5 m + LiOH 1 m
Seed	Hydrothermal	Hydrothermal	Hydrothermal	Hydrothermal	Vapor-grown	Hydrothermal
Growth temperature (°C)	355	355	355	355	355	300

to be controlled by vapor deposition. Large ZnO crystals grown by the hydrothermal method have been used previously for surface acoustic wave devices, which do not call for as high quality as optical or semiconductor device does. However, the hydrothermal method is advantageous to grow high quality and large bulk crystals if crystals grow under low super-saturation [9].

Several runs were made to obtain various single crystals. The growth parameters are listed in Table 1. The analysis of the known data and the results of our experiments showed that ZnO crystals were transparent, pale yellow, yellow, deeper yellow, green or in color depending on different growth conditions. Table 2 shows the results in coloration and amount of chemical impurities incorporated of as-grown crystals. Consider the effect of technical hydrothermal growth conditions on ZnO single crystals: ultra-pure nutrient powder resulted in colorless, NaOH resulted in deeper yellow, hydrothermal grown seeds resulted in colorless, and increase of growth temperature resulted in colorless.

The crystal growth characteristics of hydrothermal ZnO are prescribed by anisotropy between the two opposite surfaces of the basal plane as shown in Fig. 1. The opposite sides of a basal plane wafer have different atomic arrangements at their surfaces due to this anisotropy. The C^+ side comprises a Zn-rich layer, and the C^- side comprises an O-rich layer. The degree of coloration in different sectors (specified by their growth plane) might be placed in the following descending order: $(0\,0\,0\,\bar{1})$, $(1\,0\,\bar{1}\,1)$, $(1\,0\,\bar{1}\,0)$, $(0\,0\,0\,1)$ and $(1\,0\,\bar{1}\,\bar{1})$.

Although the yellow coloration appears to be associated with the Fe content (#1 in Table 2), the impurity ions content is not the unique cause as the Fe ion content in ultra-pure zinc oxide was the same and the levels of Fe ion incorporated in the crystals were similar (#2–#6 in Table 2). Other factors may also contribute to the coloration, rather than the levels of K, Na, and Li ion incorporated in the ZnO crystals. Zinc oxide defects, probably zinc interstitials, or oxygen vacancies (leading to F-type centers) were suggested as being responsible for the coloration, which could be annealed out in air to incorporate oxygen. The coloration of the present crystals was only slightly decreased by annealing in our visual examination.

Table 2
The results in coloration and amount of chemical impurities incorporated of as-grown crystals

Run	#1	#2	#3	#4	#5	#6
Coloration	Deeper yellow	Almost colorless	Yellow	Yellow	Pale yellow	Green
K (wt. ppm)	1.0	0.8	1.5	0.3	0.9	1.2
Na (wt. ppm)	0.5	0.4	0.6	2.5	0.4	0.5
Li (wt. ppm)	4.2	5.1	0.5	2.9	4.5	6.3
Fe (wt. ppm)	32	4.5	4.3	4.3	4.7	5.7

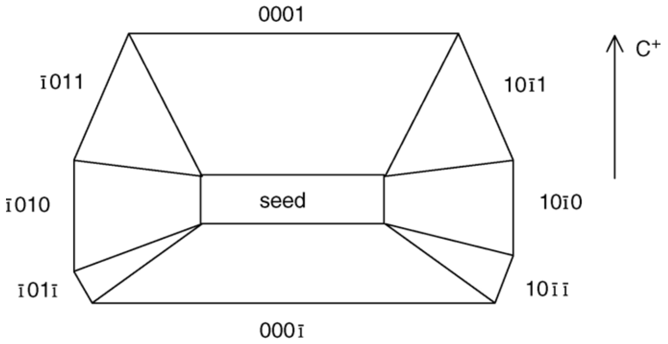

Fig. 1. Typical section through hydrothermal growth on a basal plate.

In pure KOH solutions, ZnO crystals grew at high rates (by about 1.5 times higher than in NaOH solutions). As a result, the crystals contained a larger number of intrinsic defects and were pronouncedly non-stoichiometric. High growth rates also complicated control of the growth process. Pure LiOH was too weak a solvent to provide the super-saturation necessary for growth at moderate temperatures of hydrothermal crystallization [10].

The KOH alkali is more preferable than NaOH because the larger ion radius of K^+ (K^+: $r = 0.133$ nm, Na^+: $r = 0.095$ nm) and, thus, the lower probability of its incorporation into the ZnO lattice. Intrinsic defects might be the reason that ZnO crystals were deeper yellow from NaOH solutions. The best solvents for ZnO were the mixture of KOH and LiOH solutions. The composition and concentration of mixed solutions were optimized based on the experimental data on the crystallization kinetics of zincites from 3 to 9 m KOH in the presence of 0.2–3.0 m LiOH solutions and the quality of the grown crystals.

The X-ray rocking curves for (0 0 2) reflections of ZnO single crystals under different growth conditions are shown in Fig. 2a and b. The study of the half-width in X-ray rocking curves showed an improvement in crystal quality resulted when commercial zinc oxide powder was replaced by ultra-pure material (#1, #2 in Fig. 2a), and when the lithium ion was added to the KOH solutions (#2, #3 in Fig. 2a). It also showed that ZnO crystals grown from KOH solutions, with the other conditions being the same, had better crystal structure than crystals grown from NaOH solutions (#2, #4 in Fig. 2b). Crystals grown on basal plates provided a higher proportion of colorless material and were more consistent in quality than those grown on acicular vapor-grown seeds (#2, #5 in Fig. 2b). With increase of growth temperature, the growth rate increased and the quality of the grown crystals improved (#2, #6 in Fig. 2b). The use of mixed solutions KOH and LiOH, ultra-pure materials, successive generation of seeds, and higher growth temperature allows one to grow ZnO crystals with the minimum half-width in the X-ray rocking curves, which indicates high quality of the grown crystals.

Commercial zinc oxide contains more Fe impurities than ultra-pure zinc oxide, and more Fe ion incorporated in ZnO crystals results in more oxygen vacancy defects. The effect of the addition of the lithium ion to the solutions is to retard the premature nucleation of additional growth steps during the planar growth so that growth proceeds uniformly along successive growth planes and the majority of Li atoms occupy interstitials. The quality of grown crystals continued to improve and became more reproducible as successively generated seeds were used. It is for the reason that crystllinity of the ZnO single crystals grown by the hydrothermal method is better than that of the CVT crystal [11]. Smaller scattered inclusions, probably also misoriented ZnO, which were the predominant surface defect of

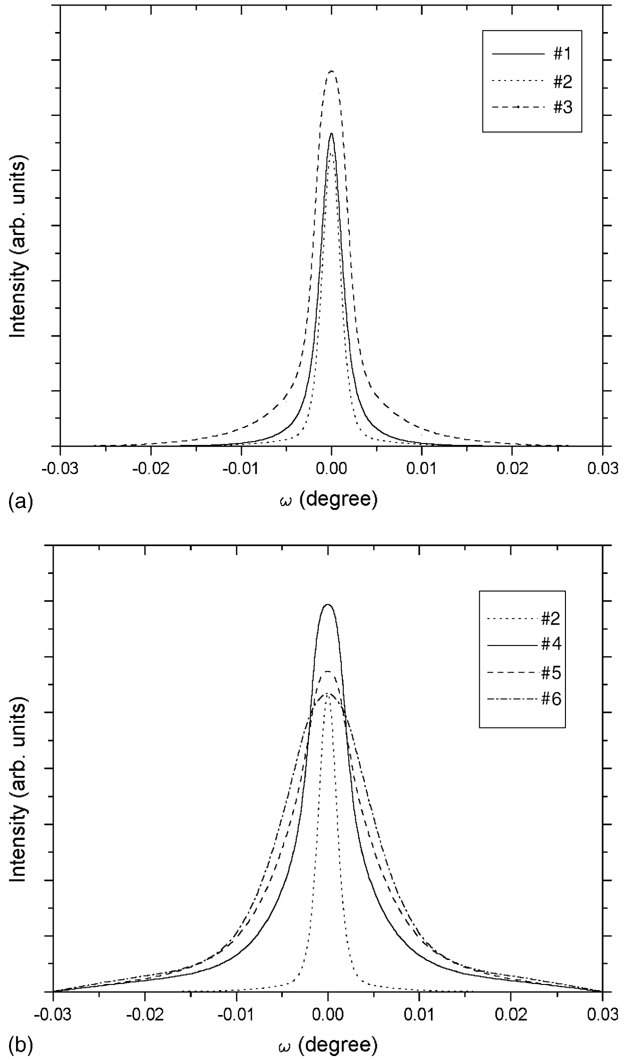

Fig. 2. (a) X-rays rocking curves for (0 0 2) reflection of ZnO single crystals (#1, #2, #3); (b) X-rays rocking curves for (0 0 2) reflection of ZnO single crystals (#2, #4, #5, #6).

vapor-phase seeds and a small number of such defects were found in early hydrothermal crystals, but none at all in later crystals. Increase of growth temperature also resulted in colorless crystals and quality improved. These effects are probably due to lattice parameters mismatch between the seeds and growth materials. The ZnO solubility in KOH and LiOH aqueous solutions increases at higher temperature. Seeds in growth regions dissolve before growth initiates. The higher the growth temperature, the more dissolves from the surface of the seeds, and the less defects residue in the surface of the seeds, and so there are fewer distortions in lattice parameter along the growth direction.

Wang et al. [12] discussed the mechanism of crystal growth in hydrothermal condition. They considered the $Zn(OH)_4{}^{2-}$ tetrahedron complex in the solution as a growth unit. This tetrahedron is slightly polarized by the displacement of Zn cation. Since the +c and −p surfaces are terminated by Zn atoms and are positively charged, tetrahedrons are easily incorporated in these surfaces with the negative basal triangle. On the other hand, the −c and +p surfaces are terminated by O atoms and are negatively charged, thus tetrahedrons are incorporated with the positively charged apex. Such differences of surfaces conditions and mechanisms of elementary process of crystal growth may be the reason for the difference of the growth rate and defect concentrations, which affected coloration. All of these results show correlation between crystal color and crystal quality.

4. Conclusions

The feasible solvents for ZnO single crystals were the mixture of KOH and LiOH solutions. All as-grown crystals were transparent, pale yellow or pale green in color. The use of ultra-pure nutrient material resulted in a sharp reduction in coloration and an improvement in crystal quality. The quality of growth continued to improve as growth temperature increased and successive generation of seeds was used. There is correlation between crystal color and crystal quality. Always high quality ZnO crystals are weak in color.

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