

Bulk ZnO: Current Status, Challenges, and Prospects

A brief overview of the recent achievements in mass production of ZnO single crystals

V. Avrutin, J.Z. Zhang, J.J. Song, D. Silversmith, *Fellow, IEEE*, and H. Morkoç

Abstract— *Rediscovered in the last decade, zinc oxide (ZnO) has attracted much attention as a promising material for many optoelectronics and to some extent microelectronics applications. However, a clear majority of effort expended in this fast developing field has been limited to heteroepitaxial structures grown on foreign substrates with lattice-parameter and thermal-expansion mismatch with ZnO which is detrimental. Recognizing the importance, the effort has shifted to include developing technologies capable of producing freestanding ZnO wafers in large-scale for ZnO based device applications, which is the subject matter of this manuscript. Three competing approaches – hydrothermal method, melt growth (modifications of the well known Bridgman technique), and seeded vapor transport growth (or sublimation) – have now reached the level which can be construed as commercialization. In this article, we discuss the progress, outstanding problems, and prospects of these growth methods employed for commercial manufacturing of ZnO wafers.*

Index Terms— Zinc oxide, single crystals, hydrothermal method, Bridgman method, vapor transport

I. INTRODUCTION

Owing to its unique electronic and optical properties, zinc oxide has attracted a great deal of interest for a variety of optoelectronics and microelectronics applications as bulk crystals, epitaxial layers, and nanostructures (see the reviews by Özgür *et al.* [1] and by Klingshirm [2]). Despite production of ZnO pellets and other freestanding templates some 4 decades ago, most of the device structures explored have so far been based on heteroepitaxial ZnO films grown on foreign substrates with lattice-parameter and thermal-expansion mismatch due to the lack of high-quality ZnO substrates. Unfortunately, the heteroepitaxial structures employed suffer from high density of threading dislocations. Furthermore, out-diffusion of electrically active Ga and Al into ZnO have been also observed for the films grown on GaN and a-plane Al_2O_3 , respectively [3]-[5]. Therefore, enormous efforts have been made towards

fabrication of large-size ZnO substrates of excellent structural perfection. A variety of ZnO substrate growth techniques are being explored, the underlying basis for which were developed in 1960's-1970's. Owing to the renewed need for large high-quality single crystals, these methods are being revamped for producing large area wafers reproducibly and economically. In this article, we will discuss the achievements and outstanding issues associated with growth techniques along with wafer properties which appear to be at the threshold of commercial production.

II. GROWTH TECHNIQUES: BASIC CHARACTERISTICS, CURRENT STATUS AND CHALLENGES

Industrial-scale growth of bulk ZnO crystals is mainly carried out by variations of the three primary methods: (a) hydrothermal [6]-[8]; (b) seeded chemical vapor transport (SCVT) or sublimation growth [9]-[11]; and (c) melt growth (two variants of the Bridgman method – pressurized melt growth employing skull melting [12] [13] and the more common approach with inductively heated Ir crucible [14]). Because of the high vapor pressure of ZnO, growth from the melt is challenging as has been the case for GaN, and the growth by vapor-phase deposition is difficult to control. In the hydrothermal method, water is used as the polar solvent, which forms metastable products with the ZnO solute (nutrient). The KOH/LiOH mineralizer is used to enhance the solubility of the nutrient. Although somewhat slow, the hydrothermal method driven by a small amount of supersaturation of the solution is viewed as a scalable process for production of large quantities of large area ZnO. However, the hydrothermally grown ZnO contains relatively large amount of K and, especially, Li incorporated from the mineralizer, which have detrimental effects on the epitaxial films grown on hydrothermal-ZnO wafers due to out-diffusion. Below we discuss basic characteristics, current status, commercial potential, and challenges facing the three aforementioned growth methods in some detail.

A. Melt growth

Melt crystal growth involves the controlled deposition of atoms onto a single-crystal seed from molten raw materials by making use of the liquid- to-solid phase transition caused by the temperature gradient. The Czochralski and Bridgman methods are the most common melt-growth techniques used for production of bulk single-crystal ingots. The Bridgman

Manuscript received April 28, 2009

V. Avrutin and H. Morkoç are with Department of Electrical and Computer Engineering, Virginia Commonwealth University, Richmond VA 23284 USA. (e-mail: hmorkoc@vcu.edu).

J.Z. Zhang and J.J. Song are with ZN Technologies, Inc., Brea, CA, USA (e-mail: jjsong@znt.us)

D. Silversmith is with Air Force Office of Scientific Research, 875 North Randolph St., Arlington (Ballston), VA 22203 (e-mail: donald.silversmith@afosr.af.mil)

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE APR 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Bulk ZnO: Current Status, Challenges, and Prospects				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research, 875 North Randolph Street, Ballston, Arlington, VA, 22203				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES U.S. Government or Federal Rights License					
14. ABSTRACT see report					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 11	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

method involves heating of the raw material in a crucible above its melting point followed by slow cooling from one end where the seed crystal is located. The temperature gradient drives the growth which starts on the seed. Single crystal material is progressively formed along the length of the vessel. The process can be carried out in horizontal or vertical geometry. In the Czochralski method, the seed crystal mounted on a rod and is dipped into the melt. The seed crystal is gradually pulled upwards while being rotated. By precisely controlling the temperature gradient, rate of pulling, and speed of rotation, it is possible to grow a large single-crystal and cylindrical ingot from the melt. The advantages of the Czochralski and Bridgman growth methods are relatively high growth rates (in the range of several millimeters per hour) and the nearly thermodynamically equilibrium conditions capable to generate bulk crystals of high structural perfection. In addition, the doping techniques are well established in these two methods. The motivation for use of the melt growth, and particularly the Czochralski and Bridgman techniques, for large scale manufacturing of single crystals lies in its cost effectiveness owing to high growth rates and high purity of resulting crystals. On the contrary, crystals grown from solutions incorporate usually traces of the solvent which is a serious drawback for electronic applications. Growth from the gas phase cannot provide sufficiently high throughput for mass production. Currently, 95% of all single-crystal silicon is grown by the Czochralski method [15]. For reference, high-purity semi-insulating GaAs used for microwave devices is grown from an As-rich melt in pressurized inert gas atmosphere with a liquid encapsulant in a variation of the Czochralski method. Si-doped n-type GaAs wafers used for optoelectronic devices are made from GaAs crystals grown by the horizontal and vertical Bridgman techniques [16]. By comparison, however, the melt growth of ZnO presents unique challenges main of which is associated with the dissociation of ZnO by $\text{ZnO} \rightarrow \text{Zn} + 1/2\text{O}_2$ reaction at the melting point, also frequently referred as the triple point. The triple point of ZnO (the temperature and pressure at which all three phases of that substance, namely gas, liquid, and solid phases, coexist in thermodynamic equilibrium) is 1975°C under the total (Zn and O_2) vapor pressure of 1.06 bar. To maintain the ZnO melt stable, the total pressure of oxygen-containing atmosphere in the growth chamber must be considerably larger than 1.06 bar. However, the design of a crucible containing molten ZnO capable of withstanding highly oxidizing conditions (temperatures of about 2000°C in oxygen containing atmosphere) is a serious challenge. Two different modification of the Bridgman technique resolving this problem, namely, pressurized melt growth with water-cooled crucible and growth utilizing iridium crucible and CO_2 atmosphere, have been proposed and implemented recently.

1) Pressurized melt growth.

The pressurized melt growth process developed by Cermet Inc. (Atlanta, Georgia) employs a modified Bridgman configuration (discussed below). This particular method produces very good quality crystals with low defect density and relatively high growth rates (1–5 mm/h) as compared to the competing techniques mentioned above. This approach

utilizes a form of melting and crystallizing materials with high melting point (above $\sim 1450^\circ\text{C}$). To be successful, these

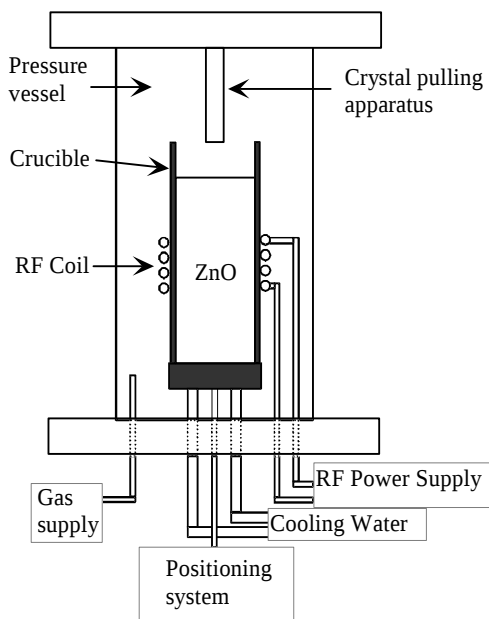


Fig. 1. A schematic illustration of the ZnO crystal growth apparatus (Courtesy of J. Nause).

materials must have a volatile component in the structure or alternatively decompose into atomic components at or near the material's melting point at atmospheric pressure. Fortunately, this is the case of ZnO allowing this particular method to be used. The vessel used is a high pressure melting apparatus wherein the melt is contained in a water-cooled crucible) under oxygen overpressure (see Fig. 1 for a simplified schematic diagram). Zinc oxide powder is used as the starting source material and melting is accomplished by radio frequency (RF) induction heating. The RF energy which produces joule heating is increased until the ZnO melts at about 1900°C . Once the molten state is attained, the crucible is slowly lowered away from the heated zone to allow controlled crystallization of the melt. The stoichiometric ZnO melt is contained in a thin layer of cooled polycrystalline ZnO formed in contact with the water-cooled crucible, which eliminates impurities which might otherwise be introduced by the crucible. Unfortunately the water-cooled crucible is the main problem associated with this technique in that the large temperature gradient induced in the melt is responsible for high stresses in the resulting ingots.

The advantages of the pressurized melt growth are high purity and commercially viable growth rates (1–5 mm/h), controlled orientation of resulting crystals (*c*, *a* or *m*-plane) made possible by the three dimensional nature of the growth, and ease of *in situ* doping control such as semi-insulating or n^+ . The material properties of the pressurized melt grown ZnO can be characterized as relatively low defect density characterized by etch-pit densities on the order of $\sim 10^4 \text{ cm}^{-2}$, an x-ray full width at half maximum (FWHM) of as low as 49 arc sec for the (0002) rocking curve [13], and very high optical quality with defect-related room temperature PL constituting approximately 0.1% of the total radiative

recombination, and approximately 85% quantum efficiency of the exciton emission [17] which is impressive. The caveat here is that this form of characterization depends very much on the excitation intensity with higher intensities favoring the band-edge emission. Highly conductive ($6.6 \times 10^{-3} \Omega\text{cm}$) Ga-doped crystals with $n = 1.3 \times 10^{19} \text{ cm}^{-3}$ and $\mu_H = 74 \text{ cm}^2/(\text{Vs})$ have been achieved recently [18]. Room-temperature electron concentration n and mobility μ_n in nominally undoped material have steadily improved and stand at $n = 4 \times 10^{16} \text{ cm}^{-3}$ and $\mu_H = 231 \text{ cm}^2/(\text{Vs})$, respectfully. The electron mobility measured at $\sim 70 \text{ K}$ is approximately $1500 \text{ cm}^2/(\text{Vs})$ [19]. Most likely the improvement of the electrical properties reflects the progress made in purification of the raw materials used for the growth of bulk crystals as discussed below. Positron annihilation experiments reported by Brauer *et al.* [20] point to the presence of Zn+O divacancies in the neutral state with a concentration of $3.7 \times 10^{17} \text{ cm}^{-3}$. By correlating the positron annihilation data with deep level transient spectroscopy (DLTS) and temperature-dependent Hall effect, it has been suggested that interstitial oxygen maybe the dominant acceptor in ZnO grown by the pressurized melt technique.

On the positive column, ZnO boules up to 50 mm in diameter have been achieved, and the growth vessel used can be scaled so that substrates with a diameter of 75 mm or larger could be obtained. In terms of the impurities, their concentration during the early developmental stage was about 19.7 ppm with primary impurities being Al, Si, Fe, Cd, and Pb, all of which come from the metallic Zn used in the preparation of ZnO source material. The improved powder source impurity levels stand at Cd (4ppm), Fe (2 ppm), Pb (5 ppm) with all others being below the detection limit. In terms of the resultant ZnO crystal chemical purity, the impurity levels are Cd (2 ppm), Fe (2 ppm), and Pb (4 ppm). The analysis for Ca showed 1 ppm both in the powder source and the resultant crystalline material [21]. However, the method is not without some undesirable characteristics, among which are the presence of low angle grain boundaries and residual strain related to the large temperature gradient related to water-cooled crucible. As a result, only a limited area of the 50-mm diameter wafers is conducive for epitaxial growth at the present time. For comparison, we should keep in mind that crystals without grain boundaries show x-ray rocking curves narrower than 50 arcsec. We should note that the concentration of vacancies also should be reduced.

2) Bridgman growth with iridium crucible.

The Bridgman method in a more common configuration, as compared to pressurized melt growth has recently made its entry into the realm of ZnO as well [14]. This technique combines the advantages of the pressurized melt growth, such as high growth rates (millimeters per hour) and nearly equilibrium conditions, with low temperature gradients ($\sim 10^\circ\text{C}/\text{cm}$ or lower) owing to the absence of water cooled crucible that, in turns, results in less stress in the growing crystals and eventually in better crystallinity. Although it was initially believed that there is no suitable material which can withstand elevated temperatures near 2000°C in oxygen-containing atmosphere the quantitative thermodynamic analysis of the Ir-Zn- O_2 system has shown that the growth in this highly reactive atmosphere should be possible with an Ir

crucible. This is because the oxidation rate of iridium exposed to elevated oxygen pressures is sufficiently low at the ZnO

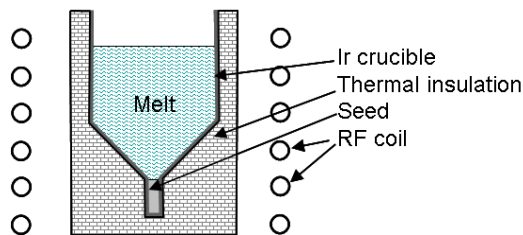


Fig.2.. Schematic of the setup for the Bridgman growth of ZnO crystals (After Ref. [14]).

melting point (1975°C) to be used as a crucible material [22], although the oxidation rate at lower temperatures, maximized in the range of $1000 - 1200^\circ\text{C}$, is intolerable. This problem is circumvented by using CO_2 atmosphere to supply the needed extra oxygen to suppress decomposition of ZnO into Zn and O_2 . At elevated temperatures, CO_2 dissociates through the reaction $\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$ with naturally a temperature-dependent dissociation rate. At temperatures around 1000°C the pressure of oxygen resulting from CO_2 dissociation is sufficiently low to avoid Ir oxidation/deterioration, but high enough to keep the ZnO melt stable at 1975°C [22].

Growth of ZnO single crystals from an inductively heated iridium crucible discussed above can be conducted in an experimental setup similar to that shown schematically in Fig. 2. The growth chamber is evacuated and then filled with either a mixture of 6 vol% CO_2 in Ar or with pure CO_2 to a pressure of 17.5 bar. The crucible with ZnO powder is heated up to the melting point of ZnO. At this temperature, the total pressure inside the growth chamber reaches approximately 19 bar. Then the electrical power is switched off and the crucible is cooled down slowly to room temperature.

Single-crystal ZnO boules of 33 mm in diameter and 40

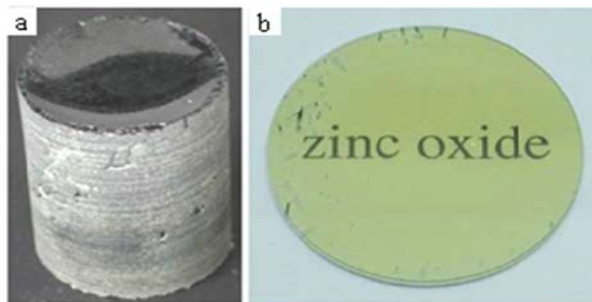


Fig.3. (a) As-grown ZnO crystal grown by the Bridgman technique and (b) a wafer 33 mm in diameter prepared from this crystal (Ref. [22]). Reprinted from J. Crystal Growth, vol. 310, no.12, D. Klimm *et al.* "The growth of ZnO crystals from the melt", pp. 3009– 3013, Copyright (2008), with permission from Elsevier.

mm in length have successfully been grown by this technique, and 33 mm diameter wafers have been cut from such boules (see Fig. 3) [23]. No discernable difference has been noted in the quality of ZnO crystals grown with pure CO_2 and CO_2/Ar mixture. The color of the as-grown crystals was either red to orange or pale green. The crystal coloration is caused by precipitates which were tentatively attributed to

zinc particles. The degree of precipitate formation was found to depend on the cooling rate. The higher the cooling rate, the higher the density of the particles is and the darker unprocessed crystals are. By a thermal treatment at approximately 1000°C the precipitates were reported to dissolve. Iridium whiskers have been found to be present only near the seed but absent in other parts as determined by chemical analysis. At the present time, it is not yet completely clear whether these whiskers disturb the growth of ZnO crystals or not. The data on the electrical and structural properties of ZnO grown by the Bridgman method available in the literature are somewhat limited, and the impurity composition has not yet been reported in sufficient detail. As grown and nominally undoped crystals show *n*-type conductivity with a free electron concentration of approximately $2 \times 10^{17} \text{ cm}^{-3}$ and electron mobility of 200 $\text{cm}^2/(\text{Vs})$ [22]. The FWHM for the (0002) x-ray rocking curves obtained from these crystals is around 22 arcsec [14]. Although this technique appears to be very promising for commercial production of ZnO bulk crystals, it is at the initial stages of development, and therefore, much remains to be done to assess its production potential fully. The electron concentration, which is a measure of background donor concentration, needs to be reduced substantially. This should be feasible by using starting materials of higher purity. It should be mentioned that the 4N (4 nines or 99.99% purity) ZnO powder was used as a starting material for the reported single crystals. Small angle grain boundaries and cracks associated with the thermal expansion mismatch between ZnO and iridium crucible are among the impediments surrounding this method [22].

B. Seeded Chemical Vapor Transport growth of ZnO

Growth of bulk ZnO crystals up to 2 inch in diameter by seeded chemical vapor transport method (hydrogen-assisted sublimation) is under development by ZN Technologies, Inc. (Brea, CA, USA). In this method, the reaction takes place in a nearly closed horizontal quartz tube. Pure ZnO powder used as the ZnO source is placed at the hot end (hot zone) of the tube which is kept at about 1150 °C. The material is transported with H_2 carrier gas to the cooler end of the reactor tube. The typical temperature difference between the evaporation zone, where the source material is, and the growth zone, where the substrate is situated, is about 50°C. This temperature differential can be varied to affect the properties of the growing crystal and the growth rate. The carrier gas is necessary because the vapor pressures of O and Zn are quite low over the ZnO source material at these temperatures. In the evaporation zone, ZnO decomposes according to the reaction $\text{ZnO(s)} + \text{H}_2(\text{g}) \rightarrow \text{Zn(g)} + \text{H}_2\text{O(g)}$. In the cooler zone, where the substrate is, ZnO is formed by the reverse reaction which is assisted by a single-crystal seed. To maintain the proper stoichiometry, a small amount of water vapor is typically added to provide the needed oxygen. A growth time in the range of 150–175 h leads to 2-in.-diameter crystals with about 1 cm in thickness (length in this case) from which can be sliced and polished into wafers. A finished ZnO slice produced in this fashion is shown in Fig. 4 (a). Fig. 4 (b) shows 12-K cathodoluminescence (CL) spectra from an

SCVT-grown ZnO wafer with chemo-mechanical polish (CMP) finish measured with different beam energies to probe

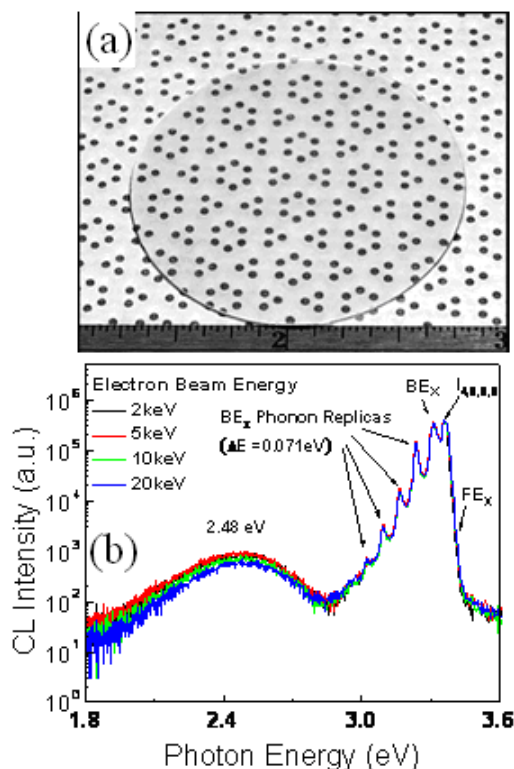


Fig.4. (a) Clear 2-inch SCVT-grown ZnO wafer with chemo-mechanical polish (CMP) finish on both faces. (b) 12-K cathodoluminescence spectra from an SCVT ZnO sample showing multiple phonon replicas, low green emission, and excellent uniformity with electron beam penetration depth which is controlled by the primary beam energy. (courtesy of Dr. L.J. Brillson).

the material properties at different depths from the surface [24]. As seen from the figure, the material is very uniform with depth. The spectra exhibit 4 phonon replicas and very low green emission which is indicative of excellent crystallinity. The SCVT grown 2" diameter ZnO wafers show high spatial uniformity of <1% determined from CL measurements [25]. Furthermore, room-temperature Hall free-electron concentration and mobility in unintentionally doped ZnO are about $6 \times 10^{16} \text{ cm}^{-3}$ and 220 $\text{cm}^2/(\text{V s})$, respectively [26]. Perhaps not the dominant impurity, hydrogen donors incorporated from the carrier gas contribute to the conductivity of SCVT-grown crystals [27]. It should be noted that the electrical properties of SCVT-grown ZnO have been treated extensively in the literature with good reproducibility of the parameters reported by different groups. Fig. 5. illustrates reproducible electron concentrations and mobilities measured for many SCVT-grown crystals. The electrical characteristics have also been found to be very uniform over the entire ingot. As an example, one ingot sampled at 16 positions yielded a net carrier concentration of $8.6 \times 10^{16} \text{ cm}^{-3}$ with a standard deviation of $0.82 \times 10^{16} \text{ cm}^{-3}$. Positron annihilation experiments show zinc vacancies, in the concentration of about $2 \times 10^{15} \text{ cm}^{-3}$ to be the dominant acceptors [28].

In general, vapor transport growth yields very pure crystals due to the inherent purification involved in the process. The

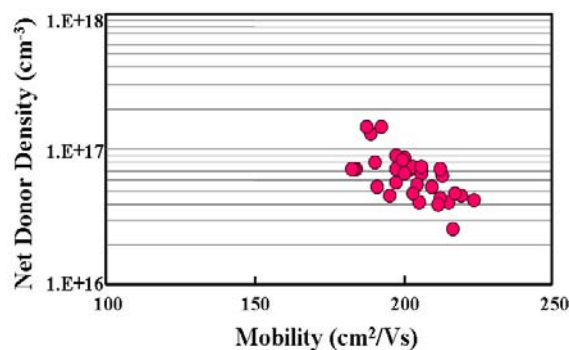


Fig. 5. Comparison of electrical properties (Hall data) for SCVT-grown ZnO single crystal ingots, illustrating the high mobility and reproducibility of the method.

chemical impurity analysis for a few wafers grown by this technique is tabulated in Table 1. Among all the techniques available for producing ZnO wafers, the SCVT method so far provides the lowest level of residual impurities which result in the highest low-temperature mobility of about 2000 $\text{cm}^2/(\text{V s})$ at $\sim 50 \text{ K}$ [29]. The very low level of known impurities in the SCVT prepared ZnO enables homoepitaxial growth without fear of contaminating the films with impurities diffusing from the substrate. This is particularly important for achieving p-type ZnO films since diffusion of n-type impurities from the substrate would be a serious obstacle.

As an ultimate test of the substrate quality and surface preparation, homoepitaxy has been successfully accomplished by both metal-organic vapor phase deposition (MOCVD) and molecular-beam epitaxy (MBE) on the Zn-face of the SCVT ZnO substrates with CMP finish. With the properly prepared surface, 2-dimensional homoepitaxial growth has been achieved by both MOCVD (atomic steps are seen in Fig. 6)

and MBE (not shown but similar) [30].

TABLE1. GLOW DISCHARGE MASS-SPECTROMETRY DATA FOR THREE DIFFERENT ZnO CRYSTALS GROWN BY SCVT. ELEMENTS NOT SHOWN IN THE TABLE HAVE NOT BEEN DETECTED DOWN TO THEIR DETECTION LIMITS.

Element	Sample A, ppma	Sample B, ppma	Sample C, ppma
B ^a	0.012	0.012	0.028
C	0.04	0.004	0.091
N ^b	0.028	0.18	0.12
Na ^b	0.015	ND	ND
Al ^a	0.009	0.007	0.020
Si ^c	0.330	0.280	0.660
Ti	0.001	ND	ND
Sn	ND	0.077	ND
Pb	0.002	ND	ND

^a Boron and aluminum are only detected n-type impurities.

^b Nitrogen and sodium are only detected p-type impurities.

^c Silicon is the major impurity consistently present. The source of Si is the quartz ampoule.

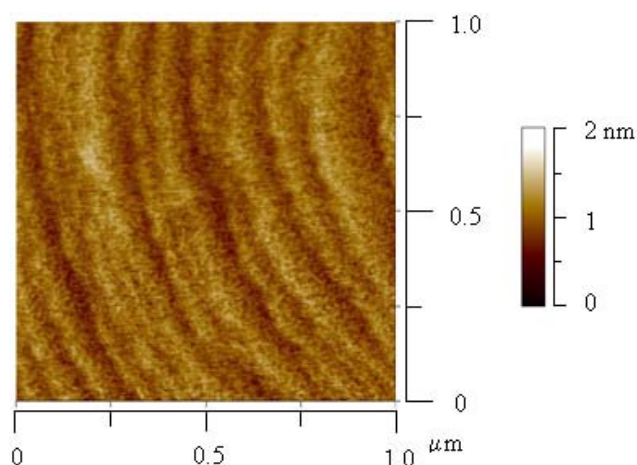


Fig.6. AFM image of a ZnO homoepitaxial film grown by MOCVD on SCVT-grown ZnO substrate. Visible features are atomic-scale steps.

While the SCVT-grown ZnO crystals often showed a large number of microvoids, stacking faults, and low-angle grain boundaries [31], progress in refinement of seeding and crystal growth has resulted in the elimination of these defects. X-ray rocking curves [(0002) reflection, $\text{CuK}\alpha$ radiation] taken at different points over the surface of a 2-inch SCVT ZnO wafer are symmetric with FWHM values ranging from 22-27 arc-seconds and peak height variations are less than 10%, indicating high crystalline quality of the wafer without indications of presence of mosaicity. As demonstrated by the growth of 3-inch ZnSe crystals, the seeded vapor transport method is capable to produce 3- and even 4-inch wafers for future market demands. Just as in other methods, the seeded chemical vapor transport technique is also accompanied by some disadvantages. The main problem is the low throughput caused by low growth rate, which together with the use of

expensive vacuum equipment would undoubtedly result in high cost for wafers. Another challenge is the establishment of doping with electrically active impurities for producing *n*- and perhaps *p*-type crystals.

C. Hydrothermal growth of ZnO crystals

As elaborated above, the hydrothermal method (more generally known as solvothermal method if non-aqueous solvents are used) lends itself to mass production of many crystals including quartz, GaN (see the article by Ehrentraut and Fukuda in this issue [32]), and also ZnO. A detail review of the hydrothermal technique for growing ZnO can be found elsewhere [33]. Below we will list the main features of this technique.

In the hydrothermal method, water is used as a polar solvent and the ZnO solute (nutrient) are placed in an autoclave which can simply be described as a pressurized vessel designed to heat aqueous solutions above their boiling point. Generally, about 70-90% of the autoclave volume can be filled [33] [34]. Fig. 7 shows the schematic of a hydrothermal growth system. The nutrient which is composed of sintered ZnO strings is dissolved in the hotter zone which is located at the bottom section of the autoclave (depicted as T_1 in Fig. 7). The aqueous solution saturated in the lower part is transported by convective motion of the solution to the upper zone housing

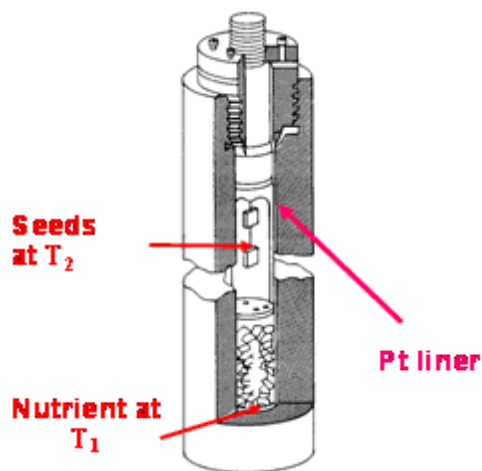


Fig.7. Schematic of autoclave for hydrothermal growth (courtesy of M. Alexander).

the ZnO seed crystals suspended by Pt wires. The upper zone is maintained at a lower temperature (depicted as T_2 in Fig. 7) to provide supersaturation. The temperature difference, ΔT , between the growth zone and the dissolution zone should be ≤ 20 K. The control over ΔT within 3 K is necessary to suppress the tendency towards spontaneous nucleation and flawed growth of ZnO.

The seeds and the particular nutrient(s) are placed into a Pt crucible [6] [35] which is also frequently referred to as the liner. Ag was used in many early attempts [36] [37], which turned out to be less resistive against corrosion in basic solutions than Pt. The use of corrosion-resistive Ti alloy liners for growing 3-inch crystals has been reported recently [34].

However, information on long-term reliability of Ti crucibles is not yet available. The crucible is sealed by welding and then placed in an autoclave which in turn is placed into a two-zone vertical furnace. The volume between the autoclave and the liner is filled with a suitable amount of distilled water for pressure balancing to prevent the liner from serious deformation. For reducing power consumption, inner heaters located between the liner and autoclave walls are also used [34]. An additional benefit of the inner heaters is that they allow enlargement of the dissolution zone that provides the needed amount of ZnO-precursor.

The hydrothermal growth of ZnO is usually performed in a temperature range from 300 to 430°C at pressures from 70 to 250 MPa. Under such conditions, water can reach the supercritical state. The critical temperature and pressure of water are 374°C and 22.1 MPa, respectively. As the temperature increases, the water density decreases while the density of water vapor increases. Above the critical point at which the densities of the liquid and vapor phases become equal, the phase boundary between the liquid and gas states ceases to exist. Further increase in temperature brings the

solvent in a supercritical state. Supercritical water exhibits an enhanced acidity, reduced density ($0.05\text{--}0.2\text{ g cm}^{-3}$), and lower polarity as compared to water kept under normal conditions. Also its diffusivity and miscibility with gases increases dramatically. The enhanced acidity favors ionic processes, such as dissolution of ZnO. However, the solubility of ZnO in supercritical water remains insufficient for the hydrothermal growth which makes the use of mineralizers necessary. Mineralizers increase the solubility of ZnO by forming metastable compounds, which later decompose at the growing crystal face to deliver Zn and oxygen which then incorporate into the ZnO lattice. LiOH, NaOH, KOH, Li_2CO_3 , and H_2O_2 have been employed as mineralizers. Pure KOH gives rise to a high growth rate but at the expense of degrading crystal quality and hindering the control over the growth process. On the other hand, LiOH alone is too weak to increase significantly the solubility of ZnO in supercritical water [38]. Consequently, the best solvent for ZnO is an appropriate mixture of KOH and LiOH. The mixture of 1M LiOH and 3M KOH water solution used for growing 2-inch single crystals [39] has been stated to generate the best crystal quality [33].

An important feature of the hydrothermal method, distinguishing it from other growth techniques, is that many seeds can be placed into a growth apparatus and, therefore, many crystals can be grown concurrently. The actual number of seeds depends on size of a growth system and desired size of resulting crystals. Choosing and preparation of appropriate seeds is a critical step for successful growth of large crystals. Spontaneously grown single crystals are used as initial seeds. The seed crystals, which are naturally larger in size, used for the next generation are cut from crystals grown from the initial seeds and. This process has to be repeated many times until the desired seed size is reached. Special measures are taken to reduce the dislocation density in the seeds [34]. Accumulation of sufficient amount of seed material for industrial-scale growth is a long and expensive process.

Unfortunately, details of the growth process as well as specific designs of autoclaves used for producing large ZnO crystals are not disclosed at present as they are considered intellectual property. However, the available data indicate that the typical growth rate of ZnO in the c^+ direction (perpendicular to the Zn-polar (0001) face) is ≤ 0.2 mm/day. This means that the growth of a 20-mm-thick 2 inch crystal from a 1-mm-thick seed 2 inch in diameter would take about 100 days. The growth rate in the c^- direction (perpendicular to the O-polar (0001) face) is 2-3 times lower [6] [37] [40]. The growth in other directions is not yet well established. Generally, the growth rates for different faces depend also on the mineralizer molar ratio [38] [41]. It is clear that optimization of the growth rate and crystal quality needs to be performed as in the case of the (0001) face.

To reiterate, the potential advantages of the hydrothermal ZnO are that it is truly a bulk growth method, and freestanding wafers up to 3 inch in diameter have been produced (Fig. 8). Despite the slow growth rates, large boules can be achieved, albeit by long process times. The process is potentially scalable to high volume production by employing large autoclaves which are capable of growing many crystals simultaneously. We should note of the scalability of the hydrothermal method to industrial levels in the realm of quartz mass production which took some 60 years to be developed and perfected. About 1850 tons of quartz were produced worldwide by the hydrothermal technique in the year 2004 alone [33]. A state-of-art large quartz autoclave can

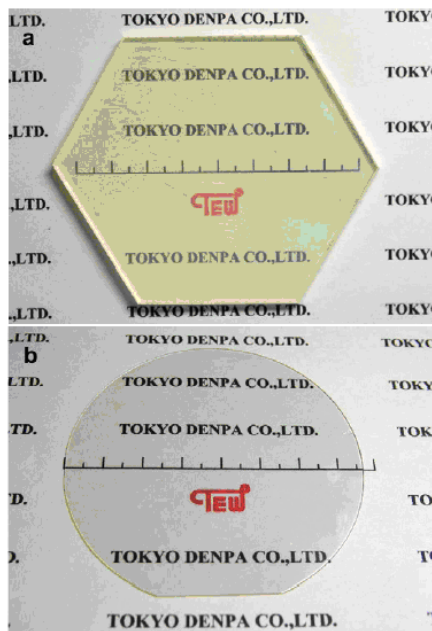


Fig.8. (a) 3-inch ZnO crystal, (b) 3 inch (0001) ZnO wafer after the CMP finish manufactured by Tokyo Denpa. Scale bar is 80 mm (Ref. [33]). Reprinted from Progress in Crystal Growth and Characterization of Materials, vol. 52, No. 4, D. Ehretraut *et al.*, "Solvothermal growth of ZnO", pp. 280-335, Copyright (2006), with permission from Elsevier.

concurrently grow more than 1400 crystals, each weighing ~ 1.7 kg, and deliver 2300 kg of the high-quality material per batch over a 100-day growth run. Although dwarfed by quartz standards, the same figures for autoclaves used for 2-inch ZnO crystals are 36 kg and about 100 crystals [30]. Nevertheless, the scale under discussion bodes well for the ZnO hydrothermal technology. Fig. 9 compares the price per cm^2 for single crystals grown by various techniques which attests to the cost effectiveness of the hydrothermal technique despite the endemic low growth rates [42]. Furthermore, high crystal quality is made possible because the material experiences no thermal stress during growth owing to low temperatures and low temperature gradients as well as slow growth rates involved.

Continuing on with other attributes of the hydrothermal growth of ZnO, low dislocation densities, eventually as low as or below 10 cm^{-2} already achieved in quartz growth, are possible. The growth takes place under conditions very close to thermodynamic equilibrium. The method has been extended beyond the binary ZnO to alloys such as ZnMgO with up to 5.5% Mg having been demonstrated by Wang *et al.* [43]. Intentional doping of the bulk material with, e.g., Al, In, N, Co has also been implemented [44] and In doping has been reported [45]. Doping with N, which should be a p-type impurity (see Avrutin *et al.*, this issue [46]), at the levels of $\sim 10^{18} \text{ cm}^{-3}$ has been demonstrated using both LiNO_3 and NH_4OH as the nitrogen precursors [47]. It was demonstrated that radiative recombination is dominated by excitonic transitions even in highly conductive crystals (up to $\sim 10^{18} \text{ electrons/cm}^3$), indicating high structural quality [48]. The growth on non-polar faces lacking polarization charge, which is advantageous in many device applications, has been

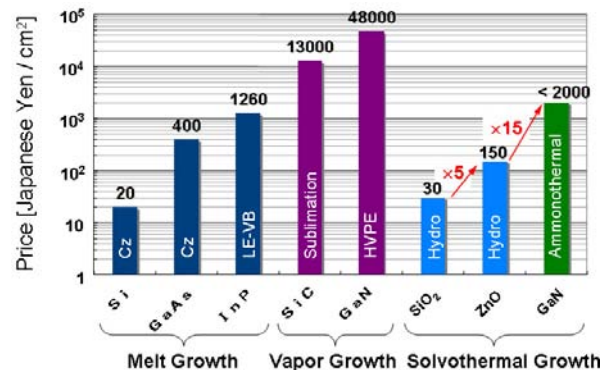


Fig.9. Normalized prices for wafers from semiconductors grown from the melt, the vapor, and from the high-pressure solution. The price for ammonothermal GaN is an estimate. (Ref. [42]). Reprinted from J. Crystal Growth, vol. 305, No. 2, T. Fukuda and D. Ehretraut, "Prospects for the ammonothermal growth of large GaN crystal", pp. 304-310, Copyright (2007), with permission from Elsevier.

demonstrated albeit not yet well established [33] [38] [41]. Finally, the hardware required for growth is essentially the same as that used for quartz growth which is very mature and readily available.

1) Current status of commercial ZnO grown by the hydrothermal method and outstanding issues.

Going beyond the virtues and woes of the method itself and focusing on the accomplishments made possible by this

method at the industrial level, excellent ~ 7.5 cm diameter c -axis single crystal substrates have been grown (Tokyo Denpa). Currently several vendors offer ZnO wafers grown by the hydrothermal technique – Tokyo Denpa (Tokyo, Japan), MTI Corporation (Richmond, CA, USA), CrysTec, GmbH (Berlin, Germany) *etc.* The characteristics indicating the very high structural quality of commercial two-inch wafers fabricated by Tokyo Denpa have been reported by Maeda *et al.* [33]. To cap them, the FWHM value of the (0002) x-ray diffraction rocking curves is about 20 arcsec and the etch-pit density is below 10^2 cm^{-2} . As revealed by X-ray topography, 2-inch wafers appear to be very homogeneous over the entire area. Furthermore, an etch pit density as low as 1 to 5 cm^{-2} has been reported by Dem'yanets and Lyutin [34] for their best 3-inch crystals. It should also be added that unintentionally doped ZnO grown by the hydrothermal technique is highly resistive (n-type): $n \leq 1 \times 10^{14} \text{ cm}^{-3}$, $\mu_n \approx 200 \text{ cm}^2/(\text{Vs})$ [36]. Low carrier concentration in hydrothermal ZnO is attributed to a high degree of compensation of shallow donors by Li acceptors incorporated from the mineralizer. In many studies, very close numbers for shallow donors and compensating acceptors (ranging from low- to mid- 10^{16} cm^{-3}) have been consistently reported for hydrothermal ZnO [19] [26] [49] [50]. As a result, conduction in bulk ZnO grown by the hydrothermal method is governed by deep donors of unknown nature [19] [51], and low temperature electron mobility does not exceed $\sim 500 \text{ cm}^2/(\text{Vs})$. Positron annihilation experiments have revealed higher concentrations of vacancy-type defects in the hydrothermal material as compared to the ZnO crystals grown by the SCVT technique [52] and the pressurized melt growth [19]. Brauer *et al.* [19] have argued that defects exhibiting a smaller open volume than the Zn vacancy, which

from the table, the total impurity concentration is relatively low and can be reduced further by using purer starting materials. The main challenge, however, is how to reduce the concentration of Li incorporation from the aqueous solution of LiOH used as a mineralizer [6]. As discussed above, Li is the main acceptor in hydrothermal ZnO compensating shallow donors, in addition to being a fast diffuser. Therefore, out-diffusion of Li from hydrothermal substrates into epitaxial structures may become a serious problem for device applications.

There is a wide dispersion in the published data on impurity concentrations in hydrothermal ZnO. As pointed out by several groups [33] [53] incorporation of impurities depends strongly on the polarity of the growing face and even the distance from the seed crystal. As an illustration, Fig. 10 shows the concentrations of Fe, Al, Li, K as functions of the distance from the seed and surface polarity measured by inductively coupled plasma mass spectrometry [33]. Negative wafer numbers (-3 to -1) indicate samples grown and cut from the c^- face and positive ones (1 to 4) refer to samples from the c^+ face of the seed crystal. Generally, the concentration of impurities decreases with increasing distance from the c^- face of the seed. This is especially obvious for Li showing 12 ppm and <1 ppm for wafer numbers -1 and -3, respectively. The concentration of K is roughly the same for both faces, standing at a level of <0.3 ppm. Fe and Al show higher concentrations in wafers grown on the c^- face of the seed. The concentrations are <11 ppm and <1 ppm for Fe and <8 ppm and <0.5 ppm for Al for the c^- face and c^+ face, respectively. For commercial ZnO wafers, however, standards dictated by the specific device applications, which are yet to be

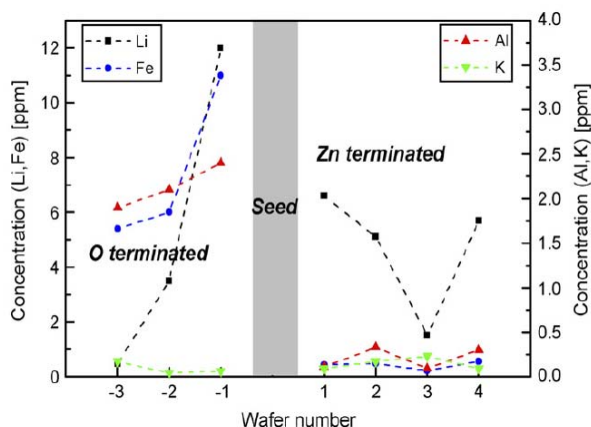


Fig. 10. Concentrations of Fe, Al, Li, and K measured by by inductively coupled plasma mass spectrometry in seven wafers cut from one crystal. Reprinted from Progress in Crystal Growth and Characterization of Materials, vol. 52, No. 4, D. Ehrentraut *et al.*, "Solvothermal growth of ZnO", pp. 280-335, Copyright (2006), with permission from Elsevier. (Ref. [33]).

could be Zn vacancies with the "attached" hydrogen, are responsible for positron trapping. The concentrations of these defects were not reported but comparison with those assessed for the SCVT and pressurized-melt crystals suggests that these values may be, at least, in the mid- 10^{17} to 10^{18} cm^{-3} range.

Table 2 summarizes the results of glow discharge mass spectrometry performed on 2-inch ZnO crystals [33]. As seen

TABLE 1. CONCENTRATION OF IMPURITIES IN 2-INCH ZNO CRYSTALS GROWN BY TOKYO DENPA MEASURED BY GLOW DISCHARGE MASS SPECTROMETRY.

Element	Concentration, ppm wt	Comments
Li	1.3	From mineralizer
Na	0.11	
K	<0.1	From mineralizer
Rb	<0.01	
Cs	<0.05	
Mg	0.330	
Ca	0.001	
Ti	<0.005	
V	<0.005	
Cr	<0.05	
Mn	<0.05	
Fe	0.06	
Co	<0.01	
Ni	<0.01	
Cu	<0.01	
Pb	<0.07	
Cd	<0.07	
Al	<0.02	
Ga	<0.05	
Si	0.18	
Ge	<0.05	
As	<0.05	
Sb	<0.5	
Pt	7.1	From liner
Lanthanides	<0.05	

developed, should be elucidated as was done for Si and GaAs wafers.

Table 3 illustrates the current status of the three main growth techniques used for bulk ZnO growth. Among the methods discussed, the material prepared by the hydrothermal method exhibits the best crystal quality in terms of full width of X-ray rocking curves (~20 arcsec for (0002) reflection) and dislocation density (state-of-art value for 3-inch crystals is $<10 \text{ cm}^{-2}$). Structural quality of 2-inch wafers is very homogeneous over the entire area. The concentration of impurities should be reduced further by using better purification of raw materials, with exception of Li (see Table 3). The main challenge for the hydrothermal method is to achieve Li-free ZnO which is no small task. As has been

shown by the large volume quartz crystal production the

TABLE 2. COMPARISON OF QUALITY OF SINGLE-CRYSTAL ZNO GROWN BY DIFFERENT METHODS.

Nominal specification	Maker	Cermet	Tokyo Denpa	ZN Technology
	Fabrication	Melt Growth	Hydrothermal	SCVT
	2"??	Yes	Yes (3")	Yes
	Grades?	Research (low) & Production (high)	Single Crystal	?
	Rocking curve (arc.sec)	42	18	32 (1 cm x 1cm)
	Impurities (ppm)	Total (< 10) Cd (2), Fe(2), Pb(4), Ca(1)	Total (< 13) Li(<12), Fe(<0.5), Al(<0.4), K(<0.2)	Total (< 0.56) Si(<0.3), N(<0.2)
	Source	Ref. [21]	Ref. [35]	

hydrothermal technique is suitable for mass production by employing large autoclaves capable to provide concurrent growth of hundreds large crystals. Another important task is the production of epi-ready wafers. In addition, doping and alloying technologies need to be improved. The competing technologies, namely the pressurized melt growth, Bridgman technique, and the seeded chemical vapor transport method, are at the developmental stages. The near term goal for the pressurized-melt growth method is to resolve the problem of grain boundaries. Although SCVT provides the lowest concentration of residual impurities, cost reduction is challenging for this techniques owing to low growth rate. In contrast to the hydrothermal technique, where growth rate is also low, only a limited number of crystals can grown in one growth system simultaneously.

III. OUTLOOK AND CONCLUDING REMARKS.

In conclusion, 3-inch ZnO(0001) wafers grown by hydrothermal technique, and 2-inch wafers produced by pressurized melt growth and seeded chemical vapor transport methods are available. With increasing demands from optoelectronics and electronics industry, the trend to increase the size of ZnO bulk crystals is expected to continue which will undoubtedly lower the prices. The hydrothermal method is now at the threshold of real mass-production of ZnO crystals. Excellent structural quality of hydrothermally grown crystals can be considered as a bench mark for the competing technologies, whereas their purity needs substantial improvement. The immediate and rather challenging task for the hydrothermal method is to reduce Li concentration, at least by one order of magnitude. At the present time, the seeded chemical vapor transport technique provides the highest purity of ZnO crystals. In terms of the throughput and thus the cost, the melt growth can potentially compete with the hydrothermal method if the problem of low-angle boundaries is resolved. As the next natural step, standards dictated by end-users of ZnO wafers should be established for surface

preparation, concentration of extended and point defects, and concentration of major electrically active impurities.

Finally, let us touch upon the challenges that are commonly faced by all ZnO growth methods. Doping technologies for mass production of n- and p-type highly conductive ZnO substrates need to be developed. P-type doping is particularly challenging task in case of ZnO. In relation with the doping problems, concentrations and types of point defects acting as donors and acceptors in bulk ZnO produced by different techniques should be assessed accurately. We should also mention that the lack of mid-gap donor/acceptors would frustrate efforts to obtain high resistivity wafers (may not be an intractable problem for high purity crystals because the band gap is large). Growth of non-c-axis crystals might need to be explored further as polarization charge in structures based on the polar c-plane in GaN, which probably will carry over to ZnO, is beginning to be viewed as a problem rather than an advantage. The effects of impurities on the growth kinetics with respect to the morphology are not well understood which need further investigations.

REFERENCES

- [1] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, and H. Morkoç, "A comprehensive review of ZnO materials and devices", *J. Appl. Phys.*, vol. 98, No. 4, pp. 041301-1 - 041301-103, Aug. 2005.
- [2] C. Klingshirn, "ZnO: from basics towards applications", *Phys. Stat. Sol. (b)*, vol. 244 No. 9, pp. 3027-3073, Sep. 2007.
- [3] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworak, U. Haboeck, and A. V. Rodina, "Bound exciton and donor-acceptor pair recombinations in ZnO", *Phys. Stat. Sol. (b)*, vol. 241, No. 2, pp. 231-260, Feb. 2004.
- [4] A. Dadgar, A. Krtischil, A. Diez, F. Bertram, J. Bläsing, J. Christen, A. Krost, in Third International Conference on Materials for Advanced Technologies, Singapore 2005, paper N-6-OR12.
- [5] V. Avrutin, M. A. Reshchikov, N. Izyumskaya, R. Shimada, S.W. Novak, and H. Morkoç, "Effect of thermal annealing on deep and near-band edge emission from ZnO films grown by plasma-assisted MBE", be published in *Mat. Res. Soc. Symp. Proc.*, vol. 1109.
- [6] T. Sekiguchi, S. Miyashita, K. Obara, T. Shishido, and N. Sakagami, "Hydrothermal growth of ZnO single crystals and their optical characterization", *J. Crystal Growth*, vol. 214-215, pp. 72-76, Jun. 2000.
- [7] N. Sakagami, M. Yamashita, T. Sekiguchi, S. Miyashita, K. Obara, and T. Shishido, "Variation of electrical properties on growth sectors of ZnO single crystals", *J. Crystal Growth*, vol. 229, No. 1, pp. 98-103, Jul. 2001.
- [8] W.-J. Li, E.-W. Shi, W.-Z. Zhong, and Z.-W. Yin, "Growth mechanism and growth habit of oxide crystals", *J. Crystal Growth*, vol. 203, No. 1-2, pp. 186-196, May 1999.
- [9] M. Shiloh and J. Gutman, "Growth of ZnO single crystals by chemical vapour transport", *J. Crystal Growth*, vol. 11, No. 2, pp. 105-109, Nov. 1971.
- [10] K. Matsumoto and K. Noda, "Crystal growth of ZnO by chemical transport using HgCl₂ as a transport agent", *J. Crystal Growth*, vol. 102, No. 1-2, pp. 137-140, Apr. 1990.
- [11] J.-M. Ntep, S. Said Hassani, A. Lusson, A. Tromson-Carli, D. Ballutaud, G. Didier, and R. Triboulet, "ZnO growth by chemical vapour transport", *J. Crystal Growth*, vol. 207, No. 1-2 pp. 30-34, Nov. 1999.
- [12] J. Nause, "ZnO broadens the spectrum", III-Vs Review, vol. 12, No. 4, pp. 28-31, Oct. 1999.
- [13] J. Nause and B. Nemeth, "Pressurized melt growth of ZnO boules", *Semicon. Sci. Technol.*, vol. 20, No. 4 pp. S45-S48, Apr. 2005.
- [14] D. Schulz, S. Ganschow, D. Klimm, M. Neubert, M. Rossberg, M. Schmidbauer, and R. Fornari, "Bridgman-grown zinc oxide single crystals", *J. Crystal Growth*, vol. 296, No. 1, pp. 27-30, Oct. 2006.
- [15] W. Zulehner, "Historical overview of silicon crystal pulling development", *Mater. Sci. Eng. B*, vol. 73 No. 1-3, pp. 7-15, Apr. 2000.
- [16] P. Rudolph and M. Jurisch, "Bulk growth of GaAs: an overview", *J. Crystal. Growth*, Vol. 198-199, Pt. 1, 325-35, Mar. 1999.
- [17] M. A. Reshchikov, X. Gu, J. Nause, and H. Morkoç, "High quantum efficiency of photoluminescence in GaN and ZnO", in *Mat. Res. Soc. Symp. Proc.*, vol. 892, pp. FF23-11.1-FF23-11.6, 2006.
- [18] J. Nause and N. Spenser, Cermet Inc., unpublished data.
- [19] G. Brauer, W. Anwand, W. Skorupa, J. Kuriplach, O. Melikhova, J. Cizek, I. Prochazka, C. Moisson, H. von Wenckstern, H. Schmidtd, M. Lorenz, and M. Grundmann "Comparative characterization of differently grown ZnO single crystals by positron annihilation and Hall effect", *Superlatt. Microstruct.*, vol. 42, No. 1-6, pp. 259-264, Jul.-Dec. 2007.
- [20] G. Brauer, W. Anwand, W. Skorupa, J. Kuriplach, O. Melikhova, C. Moisson, H. von Wenckstern, H. Schmidt, M. Lorenz, and M. Grundmann, "Defects in virgin and N+-implanted ZnO single crystals studied by positron annihilation, Hall effect, and deep-level transient spectroscopy", *Phys. Rev. B*, vol. 74 No. 4, pp. 045208-1 - 045208-10, Jul. 2006.
- [21] J. Nause (Cermet, Inc.), private communication (2008).
- [22] D. Klimm, S. Ganschow, D. Schulz, and R. Fornari, "The growth of ZnO crystals from the melt", *J. Crystal Growth*, vol. 310, No. 12, pp. 3009-3013, Jun. 2008.
- [23] D. Schulz, S. Ganschow, D. Klimm, K. Struve, "Inductively heated Bridgman method for the growth of zinc oxide single crystals", *J. Crystal Growth*, vol. 310, No. 7-9, pp. 1832-1835, Apr. 2008.
- [24] L.J. Brillson, H.L. Mosbacker, M.J. Hertzner, Y. Strzhemechny, D.C. Look, G. Cantwell, J. Zhang, and J.J. Song, "Surface and near-surface passivation, chemical reaction, and Schottky barrier formation at ZnO surfaces and interfaces", *Appl. Surf. Sci.*, vol. 254, No. 24, pp. 8000-8004, Oct. 2008.
- [25] Dr. Leonard J. Brillson, Ohio State University, unpublished data.
- [26] D. C. Look, Zinc Oxide and Related Materials, "Donors and acceptors in bulk ZnO grown by the hydrothermal, vapor-Phase, and melt processes", *MRS Symposia Proceedings*, Vol. 957 (Materials Research Society, Pittsburgh, 2007), p. 127.
- [27] D.M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov, "Hydrogen: a relevant shallow donor in zinc oxide", *Phys. Rev. Lett.*, vol. 88, No., pp. 045504-1 - 045504-4, Jan. 2002.
- [28] F. Tuomisto, V. Ranki, K. Saarinen, and D.C. Look; "Evidence of the Zn Vacancy Acting as the Dominant Acceptor in n-Type ZnO"; *Phys. Rev. B*; 91, 205502, (2003), vol. 91, No. 20, pp. 205502-1 - 205502-4, Nov. 2003.
- [29] D. C. Look, G. C. Farlow, P. Reunchan, S. Limpijumnon, S. B. Zhang, and K. Nordlund, "Evidence for Native-Defect Donors in n-Type ZnO", *Phys. Rev. Lett.*, vol. 95, No. 22, pp. 225502-1 - 225502, Nov. 2005.
- [30] Zhang, G. Cantwell, F. X. Xiu, J. J. Song, J. Zhong, and Y. Lu, "ZnO Bulk and Epi Growth for Optoelectronic Applications", in *Proceedings of GOMACTECH 2008*, Las Vegas, Nevada, March 17-20, 2008, paper No.20-3.
- [31] B.J. Coppa, C.C. Fulton, S.M. Kiesel, R.F. Davis, C. Pandarianth, J.E. Burnette, R.J. Nemanich, D.J. Smith, "Structural, microstructural, and electrical properties of gold films and Schottky contacts on remote plasma-cleaned, n-type ZnO.0001. surfaces", *J. Appl. Phys.*, vol. 97, No. 10, pp. 103517-1-13, May 2005.
- [32] D. Ehrentraut and T. Fukuda, "", this issue.
- [33] Ehrentraut, H. Sato, Y. Kagamitani, H. Sato, A. Yoshikawa, and T. Fukuda, "Solvothermal growth of ZnO", *Progress in Crystal Growth and Characterization of Materials*, vol. 52, No. 4, pp. 280-335, Apr. 2006.
- [34] L.N. Dem'yanets and V.I. Lyutin, "Status of hydrothermal growth of bulk ZnO: Latest issues and advantages", *J. Crystal Growth*, vol. 310, No. 4, pp. 993-999, Mar. 2008.
- [35] E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, and T. Fukuda, "Growth of the 2-in-size bulk ZnO single crystals by the

hydrothermal method", *J. Crystal Growth*, vol. 260, No. 1-2, pp. 166-170, Jan. 2004.

- [36] R.A. Laudise, E.D. Kolb, and A.J. Caporaso, "Hydrothermal growth of large sound crystals of zinc oxide", *J. Am. Ceram. Soc.*, vol. 47, No. 1, pp. 9-12, Jan. 1964.
- [37] Kolb, A.S. Coriell, R.A. Laudise, and A.R. Hutson, "The hydrothermal growth of low carrier concentration ZnO at high water and hydrogen pressures" *Mater. Res. Bull.*, vol. 2, No. 12, pp. 1099-1106, Dec. 1967.
- [38] L.N. Demianets, D.V. Kostomarov, I.P. Kuz'mina, S.V. Pushko, "Mechanism of growth of ZnO single crystals from hydrothermal alkali solutions", *Crystallogr. Rep.*, vol. 47, Suppl. 1, pp. S86-S98, Dec. 2002.
- [39] Maeda, M. Sato, I. Niikura, and T. Fukuda, "Growth of 2 inch ZnO bulk single crystal by the hydrothermal method", *Semicon. Sci. Technol.*, vol. 20, No. 4, pp. S49-S54, Apr. 2005.
- [40] Suscavage, M. Harris, D. Bliss, P. Yip, S.-Q. Wang, D. Schwall, L. Bouthillette, J. Bailey, M. Callahan, D.C. Look, D.C. Reynolds, R.L. Jones, and C.W. Litton, "High quality hydrothermal ZnO crystals", *MRS Internet J. Nitride Semicond. Res.*, vol. 4, Suppl. 1, G3.40, 1999.
- [41] L.N. Demianets, D.V. Kostomarov, "Mechanism of zinc oxide single crystal growth under hydrothermal conditions", *Ann. Chim. Sci. Mat.*, vol. 26, No. 1, pp. 193-198, Jan.-Feb. 2001.
- [42] Fukuda and D. Ehrentauf, "Prospects for the ammonothermal growth of large GaN crystal", *J. Crystal Growth*, vol. 305, No. 2, pp. 304-310, Jul. 2007.
- [43] B. Wang, M. J. Callahan, and L. O. Bouthillette, "Hydrothermal Growth and Photoluminescence of Zn_{1-x}Mg_xO Alloy Crystals", *Crystal Growth & Design*, vol. 6, No. 6, pp. 1256-1260, Jun. 2006.
- [44] N. Alexander (Air Force Research Laboratory Sensors Directorate, Electromagnetics Technology Division Hanscom AFB, MA), communication at communication at workshop "Challenge facing ZnO and GaN: Facts and Myths", Virginia Crossing Resort, October 18-19, 2007.
- [45] Wang, M.J. Callahan, L.O. Bouthillette, C. Xu, and M.J. Suscavage, "Hydrothermal growth and characterization of nitrogen-doped ZnO crystals", *J. Crystal Growth*, vol. 287, No. 2, pp. 381-385, Jan 2006.
- [46] V. Avrutin, D. Silversmuth, and H. Morkoç, "Doping asymmetry problem in ZnO: current status and outlook," this issue.
- [47] Wang, M.J. Callahan, L.O. Bouthillette, C. Xu, and M.J. Suscavage, "Hydrothermal growth and characterization of nitrogen-doped ZnO crystals", *J. Crystal Growth*, vol. 287, No. 2, pp. 381-385, Jan 2006.
- [48] N. C. Giles, C. Xu, M. J. Callahan, B. Wang, S. Neal, and L. A. Boatner, "Effects of phonon coupling and free carriers on band-edge emission at room temperature in n-type ZnO crystals", *Appl. Phys. Lett.*, vol. 89, No. 25, pp. 251906-1 - 251906-1, Dec. 2006.
- [49] A.Y. Polyakov, N.B. Smirnov, A.V. Govorkov, E.A. Kozhukhova, S.J. Pearton, D.P. Norton, A. Osinsky, and Amir Dabiran, "Electrical properties of undoped bulk ZnO substrates", *J. Electron. Mater.*, vol. 35, No. 4, pp. 663-669, Apr. 2006.
- [50] Z.-Q. Fang, B. Clafin, D. C. Look, and G. C. Farlow, "Electron irradiation induced deep centers in hydrothermally grown ZnO", *J. Appl. Phys.*, vol. 101, No. 8, pp. 086106-1 - 086106-3, Apr. 2007.
- [51] D.C. Look, "Unusual electrical properties of hydrothermally grown ZnO", *Superlatt. Microstruct.*, vol. 42, No. 1-6, pp. 284-289, Jul.-Dec. 2007.
- [52] Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan, and T. Sekiguchi, "Postgrowth annealing of defects in ZnO studied by positron annihilation, x-ray diffraction, Rutherford backscattering, cathodoluminescence, and Hall measurements", *J. Appl. Phys.*, vol. 94, No. 8, pp. 4807-4812, Oct. 2003.
- [53] J. Mass, M. Avella, J. Jime'nez, M. Callahan, E. Grant, K. Rakes, D. Bliss, B. Wang, "Spectrally Resolved Cathodoluminescence (SRCL) of Hydrothermal ZnO crystals", in *Mater. Res. Soc. Symp. Proc.*, vol. 878E, pp. Y1.7.1- Y1.7.6, 2005.

Vitaliy Avrutin received M.S. degree in Electrical Engineering with Honors from Moscow Institute of Steel and Alloys, Russia, and Ph.D. degree in Physics and Mathematics from Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, Russia in 1999.

He has held the positions of research engineer and research scientist at Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, Russia, and later visiting research scientist at the Department of Semiconductor Physics, University of Ulm, Ulm, Germany. In 2004, he joined the Electrical and Computer Engineering Department of Virginia Commonwealth University as research associate. His research interests are focused on epitaxial growth, characterization, and device applications of semiconductor and complex oxide thin films. He is a co-author of more than 50 papers in referred scientific journals and over 50 contributions to academic conferences and symposia. Dr. Avrutin is a member of the American Physical Society and the Materials Research Society.



Hadis Morkoç received the B.S.E.E. and M.S.E.E. degrees from Istanbul Technical University, Istanbul, Turkey, and the Ph.D. degree in electrical engineering from Cornell University, Ithaca, NY.

From 1976 to 1978, he was with Varian Associates, Palo Alto, CA, where he was involved in various novel FET structures and optical emitters based on then new semiconductor heterostructures. He held visiting positions at the AT&T Bell Laboratories (1978-1979), the California Institute of Technology, Pasadena, and Jet Propulsion Laboratory (1987-1988), and the Air Force Research Laboratories-Wright Patterson AFB as a University Resident Research Professor (1995-1997). From 1978 to 1997, he was with the University of Illinois, Urbana. In 1997, he joined the newly established School of Engineering, Virginia Commonwealth University, in Richmond, VA.

