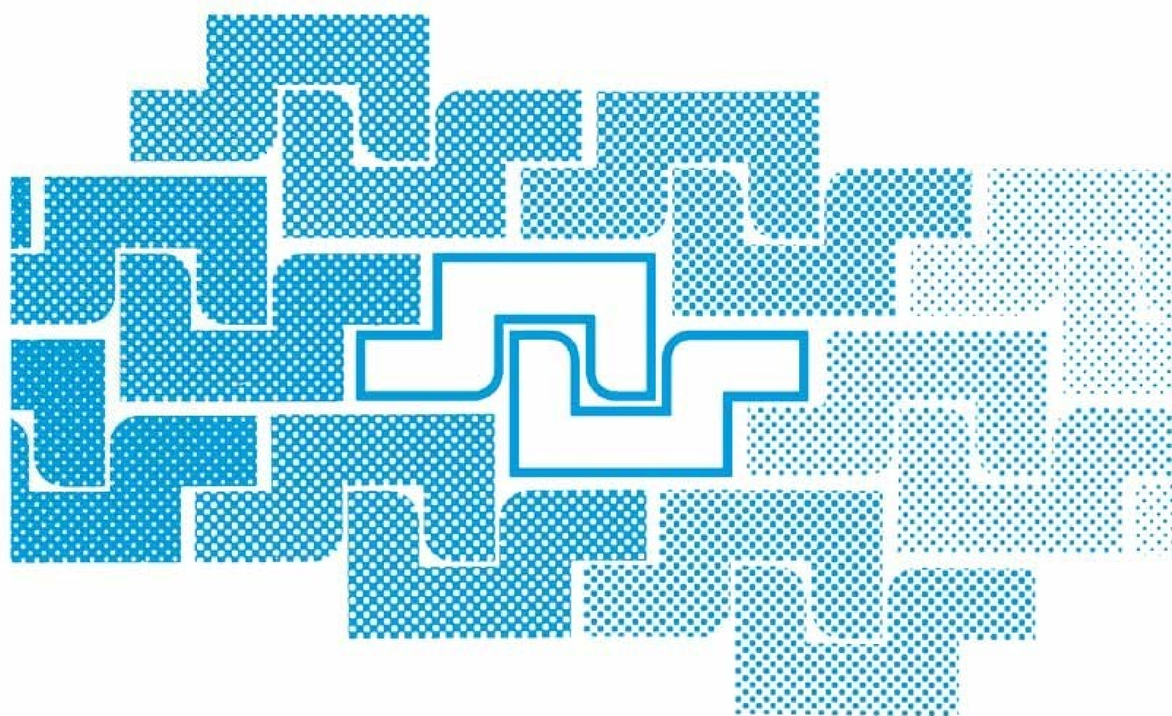

Zinc Oxide - A Material for Micro- and Optoelectronic Applications

Edited by

Norbert H. Nickel and Evgenii Terukov

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II. Mathematics, Physics and Chemistry – Vol. 194

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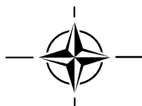

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Zinc Oxide – A Material for Micro- and Optoelectronic Applications

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Preface

Recently, a significant effort has been devoted to the investigation of ZnO as a suitable semiconductor for UV light-emitting diodes, lasers, and detectors and hetero-substrates for GaN. Research is driven not only by the technological requirements of state-of-the-art applications but also by the lack of a fundamental understanding of growth processes, the role of intrinsic defects and dopants, and the properties of hydrogen. The NATO Advanced Research Workshop on "*Zinc oxide as a material for micro- and optoelectronic applications",* held from June 23 to June 25 2004 in St. Petersburg, Russia, was organized accordingly and started with the growth of ZnO. A variety of growth methods for bulk and layer growth were discussed. These techniques comprised growth methods such as closed space vapor transport (CSVT), metal-organic chemical vapor deposition, reactive ion sputtering, and pulsed laser deposition. From a structural point of view using these growth techniques ZnO can be fabricated ranging from single crystalline bulk material to polycrystalline ZnO and nanowhiskers. A major aspect of the ZnO growth is doping. *n*-type doping is relatively easy to accomplish with elements such al Al or Ga. At room temperature single crystal ZnO exhibits a resistivity of about 0.3 Ω-cm, an electron mobility of 225 cm^2/Vs, and a carrier concentration of $\approx 10^{17}$ cm^{-3}. In *n*-type ZnO two shallow donors are observable with activation energies of 30 – 40 meV and 60 – 70 meV. It has been established that the shallower donor is interstitial hydrogen while it is believed that the deeper donor is a group IV element such as Al. On the other hand, reliable *p*-type doping is very difficult to achieve. Usually group I and group V elements are used as acceptors. So far the most common acceptor has been nitrogen because it should readily substitute for O and not distort the lattice significantly. A major problem is

the fact that most growth techniques either use hydrogen as a transport gas or H containing precursor gases such as NH_3. Therefore, in order to achieve *p*-type conductivity ZnO has to be subjected to a post-growth thermal treatment at temperatures above 650 °C. The purpose is two-fold: (i) interstitial hydrogen donors are eliminated and (ii) H passivated nitrogen acceptors are activated. The properties of H in ZnO expand well beyond the formation of donors and the neutralization of impurities and deep defects. The presence of "hidden H" has been suggested, which might be molecular H_2 that can be activated to form IR active O-H centers. Moreover, in sputtered ZnO the total H concentration can be as high as 10^{21} cm^{-3}. In addition, with increasing H concentration the average H binding energy increases; H becomes more strongly bound. Besides N, phosphorous and arsenic have been successfully used to fabricate *p*-type ZnO. Since the fabrication of *p*-type ZnO becomes more and more reliable the fabrication of *p-n* homojunction LEDs is not far off.

Recently, a new and rapidly developing area emerged, namely the field of transparent electronics based on ZnO transparent thin-film transistors. These devices exhibit an on-off ratio of 6 orders of magnitude, a channel mobility of 1 – 3 cm^2/Vs and can be fabricated at room temperature. Hence, already in the near future invisible large area electronics based on ZnO will revolutionize the electronics market. Although first small steps towards ZnO based optoelectronic applications are currently being made there is still a vast lack of fundamental knowledge regarding doping mechanisms, influence of impurities, formation of point and line defects, and their interactions with hydrogen. Some controversies and questions that arose during the workshop are based upon the fact that a materials basis for state-of-the-arte ZnO has not been established yet. Depending on the fabrication process the materials qualities such as impurities, their concentration, H content, number of point defects and grain boundaries can vary significantly.

This book reviews the latest experimental and theoretical studies in the field of ZnO. The chapters reflect the topics that were discussed during the NATO advanced research workshop, which brought together researchers from NATO countries, Russia, Ukraine, and Kazakhstan to encourage cross fertilization and wider dissemination of the advances in this important research field.

We would like to thank NATO for funding the Advanced Research Workshop. Above all, we would like to thank all participants for their interest in this workshop and active work in the vibrant field of ZnO.

Norbert H. Nickel

Evgenii Terukov

PART I: ZnO BULK AND LAYER GROWTH

Chapter 1

THE SCOPE OF ZINC OXIDE BULK GROWTH

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Abstract: The techniques classically used for the growth of bulk ZnO crystals, melt-growth, vapour growth, solution-growth and hydrothermal growth, are reviewed. In the case of vapor growth, numerical simulations suggest that such species as H_2 + H_2O, CH_4, Zn, C or Fe could act as sublimation activators. The electrical and structural properties of crystals obtained by these various techniques are compared.

Key words: ZnO synthesis, melt-growth, vapor-growth, solution-growth, hydrothermal-growth, electrical and structural properties

1. INTRODUCTION

ZnO can be considered as an 'old' semiconductor which has been compelling research attention for a long time because of its applications in many scientific and industrials areas such as piezoelectric transducers, optical waveguides, acoustooptic media, conductive gas sensors, transparent conductive electrodes, varistors.[1] It has now received increasing attention and recognized as a promising candidate for applications related to its optoelectronic possibilities in the UV range. Its piezoelectric properties could also allow developing SAW filters to be integrated in future analog circuits for portable electronic for which there is a strong need. Furthermore, ZnO transparent thin-film transistors (TTFTs) are a recent and important development in the emerging field of transparent electronics. These potential applications have boosted research related to the growth of high quality ZnO thin films by a lot of different techniques that need high quality substrates.

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That is why research related to the ZnO bulk growth has received a considerable interest during these last years.

As a result of the small ionic radii of its constituting elements, mainly the oxygen one, and of its subsequently very short and energetic chemical bond, ZnO has a very high melting point of about 1900°C. Furthermore, because of the high electronegativity of its oxygen and zinc and because of its usual off-stoichiometry, ZnO shows an extremely high reactivity with any surrounding material at high temperature. This intrinsic property will be shown to affect strongly its growth, not only its melt-growth but also its vapour-growth.

In this chapter, the various techniques classically used for the growth of bulk ZnO crystals will be reviewed.

2. ZINC OXIDE SYNTHESIS

It is worth noting that ZnO occupies already an enviable place in the industrial market. Tens of thousands tons of ZnO powder are industrially produced each year which are used in the rubber industry as vulcanisation activator (~36 %), in the industry of ceramics as a flux (~26 %), in the chemical industry (desulphuration of gases, fabrication of stearates, phosphates. etc) (~20 %), as trace elements in the animal food (~12 %), in the paints (~3 %; 50 % in 1961!). The last ~3 % are used for different applications, in electronics (ferrites, varistors), ends of matches, pharmaceutic industry (fungicidal properties of ZnO for skin-problems, trace elements ...etc.).

ZnO powder is produced from the combustion of vapors coming from the distillation of metallic zinc according to the so-called French process or dry process. Using vapors coming from fractionated distillation, extra-pure oxide powders are produced, as illustrated from the chemical analysis data of two kinds of powder produced by two different companies:

‘pharmacy B’ grade, produced by Union Minière: Pb<20 ppm, Cd<10ppm, Fe<5 ppm, Cu<1 ppm.

‘colloidal’ grade, produced by Silar SA: Pb<20 ppm, Cd<30 ppm, Fe<5 ppm, Cu<2 ppm, Mn<2 ppm.

The grain size can change according to the variety considered.

3. ZINC OXIDE MELT-GROWTH

In spite of its very high melting-point (~ 1900°C) and very high reactivity with any surrounding material at high temperature, large ZnO bulk are grown from the melt at Cermet, Inc., Atlanta, GA, using a patented pressurized melt growth process.[2,3] The technique uses a high-pressure induction melting apparatus, wherein the ZnO melt is contained in a water-cooled crucible. The whole melting and containment process is carried out in under a controlled oxygen overpressure close to 50 atm preventing the decomposition of the compound into atomic species and establishing a thermodynamic equilibrium between the liquid ZnO and the oxygen pressure, thereby preventing reduction of the lattice. The molten charge is somewhat contained in a ZnO liner, because the cooled material in contact with the cold-wall crucible constitutes a solid thermal barrier. This prevents the molten material from coming into direct contact with the cooled surface and solves the problem of the extreme reactivity of ZnO with any crucible material at high temperature. This allows furthermore to get rid from any contamination from the crucible material. 5.5-inch-diameter, kilogram sized ingots have been reported to be grown.[3] But the drawback of the technique lies in the concave liquid/solid growth interface, as a result of the cold-wall crucible, which makes it difficult to get a large grain size.

4. ZINC OXIDE VAPOR GROWTH

Because of the high melting-point of ZnO, there have been many attempts of growth of ZnO single crystals in the vapor phase.

Small crystals have been obtained by chemical vapour transport (CVT) in closed tubes using such chemical transport agents as Zn, $ZnCl_2$, ammonium halides (NH_4X), HCl, Cl_2, NH_3, NH_4Cl, $HgCl_2$, H_2, Br_2, at source temperatures ranging from 800 to 1150°C and ΔT from 20 to 200°C.[4-8]

Crystals of small size have been grown as well in open tube systems, either by oxidation of ZnI_2,[9] ZnS, ZnSe,[10] $ZnBr_2$[11] and Zn[12-14] or by hydrolysis of ZnF_2,[15] $ZnCl_2$,[16,17] ZnI_2.[18] The oxidation or hydrolysis character of the reaction can depend on the temperature range used for a same source. The temperature of the growth region ranges generally from 900 to 1350°C.

This field of research on the vapor-growth of ZnO has been reactivated from ~ 1998 by the need of ZnO substrates for growing epitaxial structures in view of photonic applications.

Large diameter (2-inch diameter) boules have been reported to be grown at Eagle Picher at 1000-1200 °C by seeded chemical vapor transport (SCVT) in a nearly closed horizontal tube using H_2 as a carrier gas and a small

amount of water to maintain the proper stoichiometry:[19] The crystals are seeded at full diameter; the source/substrate distance is of about 3 inches; the stoichiometry is controlled from the presence of a residual water pressure; the growth rates are of about 40 μm per hour. 2-inch diameter crystals of about 1-cm-thickness are produced after 150-175 h; the etch pit (dislocation) density is of about 10^4 cm^{-2}; the X-ray double diffraction rocking curve FWHM is of about 40 arcsec, with some scattering indicating the presence of residual strains. GDMS analysis reveals the purest material ever done by Eagle Picher. The crystals are of *n*-type with $n \sim 8\times10^{16}$ cm^{-3} and $\mu \sim 150\text{-}350$ cm^2/Vs @ RT. The homoepitaxial growth of ZnO on such substrates has been achieved on <0001> Zn faces chemo-mechanically polished. The future goal is the growth of larger diameter substrates, up to 3 inch.

Centimeter-size single crystals with rocking curve FWHM ~ 28 arcsec have been obtained using C or CH_4 as a transporting chemical agent.[20, 21]

ZnO, ZnO:Mn and $Zn_{1-x}Mn_xO$ ($x<0.05$) crystals were grown by CVT as well using hydrogen or nitrogen or chlorine and a little of water and carbon as a transporting agent.[22]

We had observed that a weak sublimation only occurred in a classical Piper and Polich configuration when using ampoules sealed under vacuum or filled with pure dry hydrogen with the material charge at 1000-1030°C and the top of the ampoule at 950°C. When such gases and gas mixtures as H_2+H_2O or Ar are introduced in the ampoules, fast transport to the cold point was observed, demonstrating the activator role of theses gases and gas mixtures.[23]

Given the fact that the free enthalpy of the reactions: $ZnO + H_2 \leftrightarrow Zn + H_2O$ and $ZnO + H_2O \leftrightarrow Zn + H_2 + O_2$ are positive and that such reactions cannot consequently occur towards the right-hand side, we have tried to investigate the actual mechanisms of the “CVT” transport with hydrogen and other species both from close-spaced vapor transport (CSVT) experiments and from a numerical modeling.

4.1 CSVT experiments

CSVT allows short experiments and easy determination of the growth rate. In this technique, a source and a substrate are placed at very short distance (~ 1mm). The experiments were achieved under a hydrogen flow of 1 l/min at two source temperatures, 550 and 600°C. In Fig. 1 is pictured the instantaneous growth rate as a function of the inverse substrate temperature for these two source temperatures. The solid and dashed lines correspond to a fit using a theoretical model.[23, 24]

From this fit, the enthalpy of formation has been calculated and found abnormally small, with a value of 0.42 eV, more than three times lower than

the one found for ZnSe. Furthermore, the variation of the instantaneous growth rate as a function of time has been found to be non-linear, as shown in Figure 2.

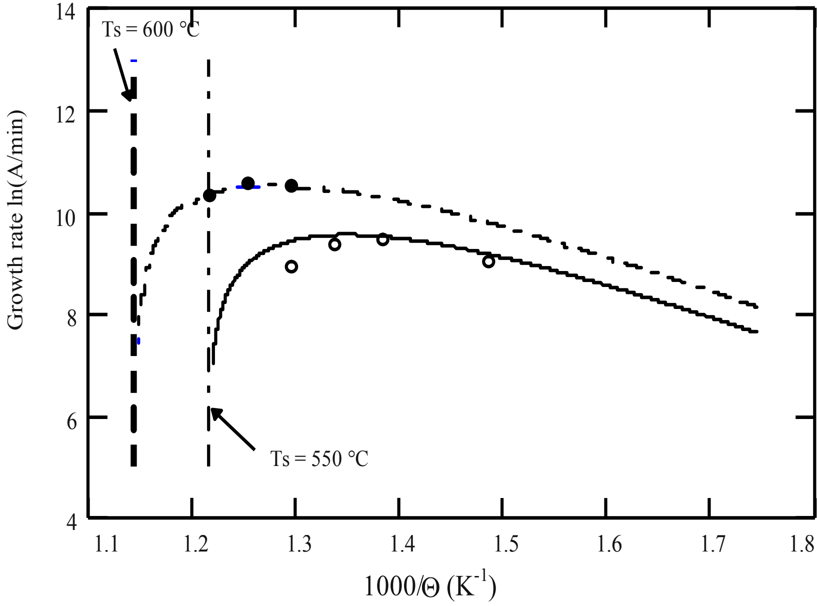

Figure 1. ZnO instantaneous growth rate as the function of the inverse source temperature for two source temperatures, 550°C and 600°C.

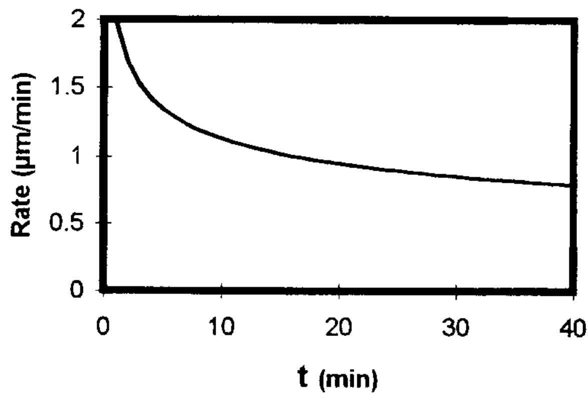

Figure 2. Instantaneous growth rate as a function of time.

From this variation of the growth rate with time and from the small ΔH value, compared to the ZnSe one, we suggested that the vapor growth of ZnO with hydrogen occurred according to a complex chemically assisted sublimation mechanism involving a competition between two different mechanisms, one associated with ZnO, the other with Zn.

4.2 Numerical simulation

In addition to this "chemically assisted" sublimation suggested with such gaseous mixtures like H_2 + H_2O, acting as "sublimation activators", several experimental observations have led us to undertake a numerical simulation of the transport.[25] While no sublimation has been found to occur in closed ampoules under vacuum conditions, high vapor transport rates are observed not only with gases like H_2 + H_2O or CH_4 but also if some particular additional species like Zn, C or Fe are introduced in the ampoule.

A simple experimental set-up consisting in a horizontal ampoule of diameter D and length L with the source material at one end and the growing crystal at the other one has been taken into account for the simulation.[25] The source and crystal temperatures are T_S and T_C respectively and the ampoule wall being subjected to a given temperature profile. We consider a PVT process in which, after ZnO decomposition, the O_2 (g) and Zn (g) are treated as two species transported in a residual gas considered as inert. These species combine at the crystallization interface giving ZnO. The involved mechanism of decomposition and crystallization being unclear, we focus only on transport phenomena. Following previous numerical studies of the mass transport process on II-VI materials,[26] surface reactions are taken into account via the partial pressures of compounds at interfaces by using the equilibrium constant and experimental data, if known, for the stoichiometric coefficient. The governing equations for the vapor transport are the conservation equations for momentum, heat and mass transfer. For the numerical resolution of the conservation equations, the computational code FLUENT has been used. The simulation has shown that if equilibrium partial pressures at interfaces are considered, the growth can only occur for a reduced interval of residual gas pressure (~10^{-3} atm). Fig. 3 shows that mass fluxes through both interfaces are only similar for a narrow subinterval of total pressures around 10^{-3} atm. Partial pressures of species, mainly Zn, higher than those corresponding to the congruent sublimation ("equilibrium pressures") are required to obtain an effective mass transport in a wide interval of total pressures. The generation of such pressures higher than the equilibrium ones becomes a limiting step in the transport of ZnO by vapor transport. This behaviour suggests the presence of an "activated" mechanism

in the ZnO decomposition, as proposed in the CSVT approach. Some kind of "autocatalytic" process is induced from the reaction of ZnO with such species as $H_2 + H_2O$, H_2O, Zn, C, CO, CH_4 or Fe resulting in the generation of an excess of Zn.

Searching for a mechanism that could justify these high pressures, we have suggested that:

A plausible mechanism could be the autocatalytic role of Zn that, by means of a surface reaction, would reduce the activation energy of the ZnO decomposition and would generate partial pressures higher than those at equilibrium.

The role of some additional species as Zn, Fe, Cu, C and H_2, in the ZnO growth by vapor transport, can be interpreted in this framework. These species would produce a Zn excess, either directly or from an O_2 consumption.

This "autocatalytic" mechanism paves the way to new processes to promote the growth of ZnO by vapor transport using the generation of an additional Zn vapor pressure and limiting the off-stoichiometric effects by controlling it.

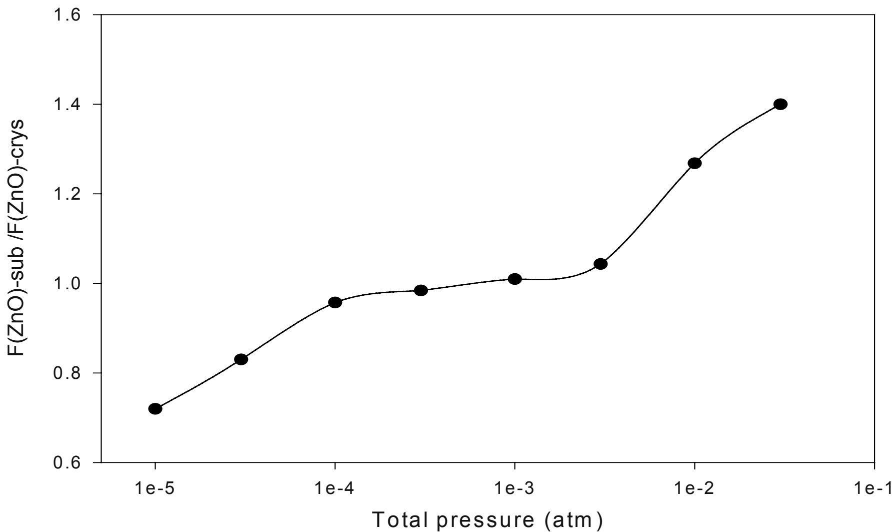

Figure 3. Calculated ratio between ZnO mass fluxes at both interfaces as a function of total pressure under equilibrium conditions.

5. ZINC OXIDE SOLUTION GROWTH

Such solvents as PbF_2[27] and V_2O_5/P_2O_5 mixtures[28] have been used for the flux growth of ZnO crystals. Using PbF_2 as the solvent in sealed Pt crucibles, ZnO crystals have been grown by THM.[29] $PbCl_2$ has been found to be a very good solvent of ZnO as well, but showing also great reactivity with any surrounding material but platinum.[30] The same authors have found the Zn-In alloys to be good solvents of ZnO without reactivity with silica. NaCl has been found recently to be an excellent solvent of ZnO allowing solution-growth in silica at temperatures of about 900°C.[31] Figure 4 pictures a ZnO crystal grown using NaCl as a solvent.

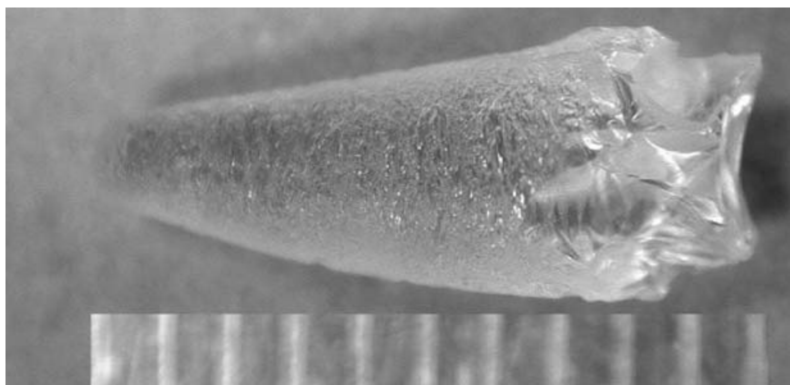

Figure 4. ZnO crystal grown using NaCl as a solvent.

6. ZINC OXIDE HYDROTHERMAL GROWTH

Hydrothermal-growth is usually defined as the use of an aqueous solvent at elevated temperature and pressure to dissolve a solute which would be insoluble under ordinary conditions. The advantages of the hydrothermal technique are a low growth temperature, a ΔT close to 0 at liquid/solid interface, an 'easily scalable' technique, the reduction of most of the impurities from source. The disadvantages are the presence of intermediate products, the lithium or sodium or potassium incorporation when such solvents as LiOH, NaOH or KOH are used, the slow growth rates (~10 mils per day), the inert liner needed, the occasional incorporation of OH and H_2O.

The first experiments on ZnO crystal growth by the hydrothermal method began in the early sixties, both in Bell Telephone Laboratories and in the Institute of Crystallography of the USSR Academy of Sciences. The