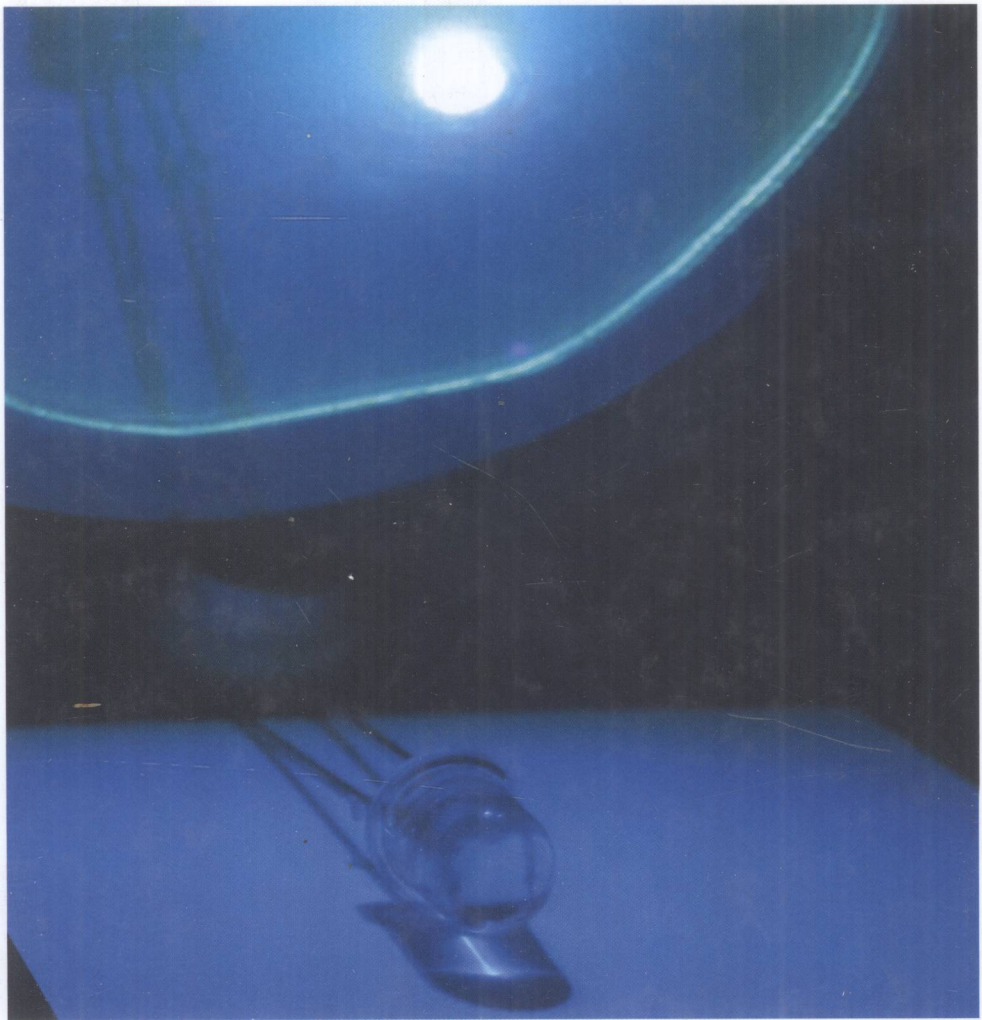
Hadis Morkoç and Ümit Özgür

WILEY-VCH

Zinc Oxide

Fundamentals, Materials and Device Technology



Hadis Morkoç and Ümit Özgür

Zinc Oxide

Fundamentals, Materials and Device Technology

WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Dr. Hadis Morkoç
Virginia Commonwealth University
Dept. of Electrical Engineering
Richmond, VA
USA

Ümit Özgür
Virginia Commonwealth University
Dept. of Electrical Engineering
Richmond, VA
USA

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

Typesetting Thomson Digital, Noida, India
Printing betz-druck GmbH, Darmstadt
Binding Litges & Dopf GmbH, Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-40813-9

Hadis Morkoç and Ümit Özgür
Zinc Oxide

Related Titles

Neumark, G. F., Kuskovsky, I. L., Jiang, H. (eds.)

Wide Bandgap Light Emitting Materials And Devices

2007

ISBN: 978-3-527-40331-8

Capper, P., Mauk, M. (eds.)

Liquid Phase Epitaxy of Electronic, Optical and Optoelectronic Materials

2007

ISBN: 978-0-470-85290-3

Preface

The semiconductor ZnO has gained substantial interest in the research community in part because of its large exciton binding energy (60 meV) that could lead to lasing action based on exciton recombination and possibly polariton/exciton interaction even above room temperature. The motivation for this book stems from the applications of ZnO in potential optical devices, transparent ohmic contacts, light extraction enhancement structures for GaN-based light-emitting diodes (LEDs), transparent thin-film transistors, transducers, and so on, for which ZnO is well suited.

We should mention that even though research focusing on ZnO goes back to many decades, the renewed interest is fuelled by the availability of high-quality substrates and reports of p-type conduction and ferromagnetic behavior when doped with transition metals, both of which remain controversial. The lattice parameter studies date back to 1935 [1], vibrational properties were studied by Raman scattering in 1966 [2], detailed optical properties were investigated in 1954 [3], and its growth by chemical vapor transport was attained in 1970 [4]. In terms of devices, Au Schottky barriers were formed in 1965 [5], LEDs were demonstrated in 1967 [6] wherein Cu2O was used as the p-type material, metal insulator semiconductor (MIS) structures were reported in 1974 [7], ZnO/ZnTe n–p junctions were accomplished in 1975 [8], and Al/Au ohmic contacts were reported in 1978 [9]. Very high quality what used to be called whiskers and platelets, the nomenclature that gave way to nanostructure, of late, have been prepared early on and used to deduce much of the principal properties of this material, particularly the optical properties, albeit with a healthy debate about the valence band ordering and assignment of some of the peaks appearing in optical excitation measurements. In addition to the requisite direct bandgap, the attraction to ZnO can simply be attributed to its large exciton binding energy of 60 meV, which might potentially pave the way for efficient room-temperature exciton-based and/or polariton/exciton interaction-based lasers with very low-threshold currents. The field is also fuelled by theoretical predictions and perhaps experimental confirmation of ferromagnetism at room temperature for potential spintronics applications. Of paramount importance is the transparency of ZnO to visible light that is in part responsible for exploring this material for applications such as transparent ohmic contacts for light emitters based on GaN, solar cells that have been gaining considerable interest, transparent thin-film transistors, and nanostructures that can be used to extract light from LEDs such as those

Zinc Oxide: Fundamentals, Materials and Device Technology. Hadis Morkoç and Ümit Özgür

ISBN: 978-3-527-40813-9

based on GaN. Furthermore, highly piezoelectric nature of ZnO and its favorable electromechanical coupling coefficient are very attractive for devices such as surface acoustic waves.

This book is unique in the sense that it represents the first cohesive treatment of the entire field of ZnO and related materials and devices under one cover. As such, much needed continuity and smooth flow are provided without duplications. The aspects of ZnO forming the basis for this book are presented in eight chapters, the contents of which are elaborated on below.

Chapter 1 treats the mechanical–thermal, chemical, and electrical properties of ZnO. Low-field as well as high-field transport is discussed. Chapter 2 discusses the growth of ZnO and heterostructures by popular techniques such as sputtering, molecular beam epitaxy, pulsed laser deposition, and chemical vapor deposition. Substrates on which ZnO is deposited along with resultant properties of the material are also discussed. Chapter 3 provides the most comprehensive treatment of optical properties of ZnO that are rich not only in terms of linear processes but also in terms of nonlinear processes. In this vein, following an introduction to optical processes in semiconductors, the specifics of optical transitions related to free excitons and polaritons, bound excitons, two-electron satellite transitions are treated in detail. This segues into the discussion of defect-related transitions such as the celebrated green, yellow, and red transitions. After discussing the refractive index of ZnO and its ternary ZnMgO, a detailed discussion of stimulated emission in ZnO is given, including single-crystal and polycrystal forms and quantum wells. The treatment then moves on to the discussion of recombination dynamics looking at the recombination lifetimes. The attention is then turned onto nonlinear optical properties including second- and third-order harmonic generation, intensity-dependent refractive index, and two-photon absorption.

Chapter 4 discusses the all-important doping in ZnO, in particular p-type doping. Details and motivations for approaches taken for attaining p-type conductivity inclusive of codoping methods and characterization schemes are provided. Chapter 5 deals with doping ZnO with magnetic ions in the context of dilute magnetic semiconductors. A sufficient amount of the theory of magnetization, classification of magnetic materials, measurement techniques, and theoretical and experimental investigations of magnetic ion-doped ZnO such as Mn and Co, among others, are discussed.

Chapter 6 discusses bandgap engineering that forms the basis for many of the high-performance electrical and optical devices based on semiconductors. ZnO alloyed with Mg and Be for increasing its bandgap and alloyed with Cd for decreasing its bandgap is discussed with the accompanying issues with regard to changes in the lattice constant and of course the bandgap. Chapter 7 paves the way for nanostructures based on ZnO. After the discussion of most popular nanostructure fabrication techniques, the application of these techniques to ZnO nanostructures such as nanorods (nanowires), nanobelts, and polypod systems is discussed.

The book ends with the discussion of ZnO processing needed for devices, metal semiconductors contacts and their current–voltage relationships including the fundamentals of current conduction mechanisms in various regimes, etching of

ZnO, and heterostructure devices. Among the devices, light emitters, microcavities, optically pumped lasers, photodiodes, metal–insulator–semiconductor diodes, field-effect transistors, transparent conducting oxides, and transparent thin-film transistors based on ZnO, piezoelectric devices in the form of surface acoustic wave devices, and gas and biosensor followed by solar cells cap the discussion.

It is not only fair but gratifying to state that we owe so much to so many including our family members, friends, coworkers, colleagues, and those who contributed to the field of semiconductors in general and ZnO in particular in our efforts to bring this manuscript to the service of readers. To this end, HM would like to thank his wife Amy and son Erol for at least their understanding why he was not really there for them fully during the preparation of this manuscript, which took longer than most could ever realize. UO wants to thank his parents and his sister for their continuing support throughout his career. Also, without the support of VCU, our past Dean R.J. Mattauch and current Dean R.D. Jamison, past assistant Dean Susan Younce, Department Chair A. Iyer, and our coworkers and students, it would not have been possible to pursue this endeavor.

Special recognitions also go to our coworkers Dr Y.I. Alivov, Dr V. Avrutin, Dr N. Izyumskaya, and Professor M. Reshchikov for their contributions to the research that made possible the discussions on growth, devices, and point defects a much more manageable task.

Special thanks go to J.M. Recio, S. Desgreiners, J. Pollmann, J.E. Jaffe, F. Decremps, M. Schubert, C. Bundesmann, N. Ashkenov, T. Sekiguchi, T. Fukuda, J.-J. Song, J. Nause, P. Ruterana, Q. Wang, Y. Chen, T. Yao, K. Thonke, C. G. van de Walle, P. Dahan, B. Meyer, S.-J. Park, A. Krost, X. Feng, T. Fukumura, Y.-H. Jeong, G. Lawes, I. Tanaka, D.P. Norton, N.H. Hong, J.M.D. Coey, M.H. Kane, T.-S. Chin, Y. Ishida, K. Ando, A. Ohtomo, T. Makino, P. Yang, Z.L. Wang, A.B. Djurišić, G.-C. Yi, B.P. Zhang, M. Kawasaki, R. Shimada, D. Hofstetter, Y. Lu, S. Fujita, N.H. Nickel, B. Gil, R.L. Hoffman, J. Fallert, and C.K. Klingshirn for willingly devoting considerable time and effort to provide us with digital copies of figures and high-quality images. They are also acknowledged in conjunction with the figures.

Richmond, VA, June 2008 *Hadis Morkoç and Ümit Özgür*

References

1 Bunn, C.W. (1935) *Proceedings of the Physical Society*, **47**, 835.
2 Damen, T.C., Porto, S.P.S. and Tell, B. (1966) *Physical Review*, **142**, 570.
3 Mollwo, E. (1954) *Zeitschrift fur Angewandte Physik*, **6**, 257.
4 Galli, G. and Coker, J.E. (1970) *Applied Physics Letters*, **16**, 439.
5 Mead, C.A. (1965) *Physics Letters*, **18**, 218.
6 Drapak, I.T. (1968) *Semiconductors*, **2**, 624.
7 Minami, T., Tanigava, M., Yamanishi, M. and Kawamura, T. (1974) *Japanese Journal of Applied Physics*, **13**, 1475.
8 Tsurkan, A.E., Fedotova, N.D., Kicherman, L.V. and Pas'ko, P.G. (1975) *Semiconductors*, **6**, 1183.
9 Brillson, L.J. (1978) *Journal of Vacuum Science & Technology*, **15**, 1378.

Contents

Zinc Oxide: Fundamentals, Materials and Device Technology. Hadis Morkoç and Ümit Özgür

ISBN: 978-3-527-40813-9

1
General Properties of ZnO

In this chapter, crystal structure of ZnO encompassing lattice parameters, electronic band structure, mechanical properties, including elastic constants and piezoelectric constants, lattice dynamics, and vibrational processes, thermal properties, electrical properties, and low-field and high-field carrier transport is treated.

1.1
Crystal Structure

Most of the group II–VI binary compound semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite (Wz) structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp^3 covalent bonding nature, but these materials also have a substantial ionic character that tends to increase the bandgap beyond the one expected from the covalent bonding. ZnO is a II–VI compound semiconductor whose ionicity resides at the borderline between the covalent and ionic semiconductors. The crystal structures shared by ZnO are *wurtzite* (B4), *zinc blende*[1] (B3), and *rocksalt* (or Rochelle salt)[2] (B1) as schematically shown in Figure 1.1. B1, B3, and B4 denote the *Strukturbericht*[3] designations for the three phases. Under ambient conditions, the thermodynamically stable phase is that of wurtzite symmetry. The zinc blende ZnO structure can be stabilized only by growth on cubic substrates, and

1) The term zinc blende originated from compounds such as ZnS, which could be in cubic or hexagonal phase. But the term has been used ubiquitously for compound semiconductors with cubic symmetry. The correct term that should be used for the cubic phase of ZnO GaN is actually *sphalerite*. To be consistent with the diction throughout the literature even at the expense of bordering inaccuracy, the term zinc blende is used throughout this book.

2) Also called Seignette salt – named after Pier Seignette from La Rochelle, France, who first prepared potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6{\cdot}4H_2O$) in 1675 and determined its structure.

3) *Strukturbericht*, the original crystallographic reports. From 1919 to 1939 (Vols 1–8), they were published in Germany. Since then, they have been published in the United States under the name *Structure Reports, Acta Crystallographica Section E*, by the International Union of Crystallography.

Zinc Oxide: Fundamentals, Materials and Device Technology. Hadis Morkoç and Ümit Özgür

ISBN: 978-3-527-40813-9

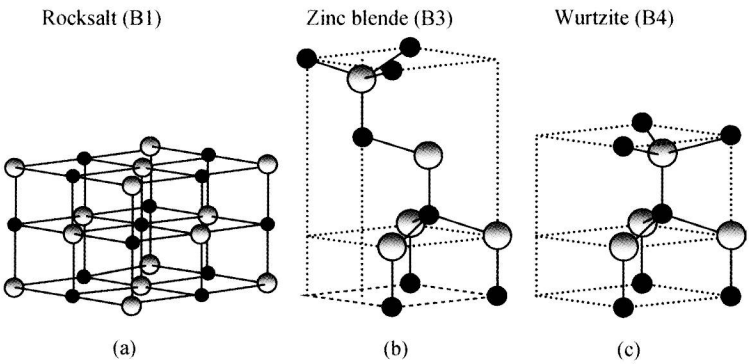


Figure 1.1 Stick-and-ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). Shaded gray and black spheres denote Zn and O atoms, respectively.

the rocksalt or Rochelle salt (NaCl) structure may be obtained at relatively high pressures, as in the case of GaN.

The *wurtzite* structure has a hexagonal unit cell with two lattice parameters a and c in the ratio of $c/a = \sqrt{8/3} = 1.633$ (in an ideal wurtzite structure) and belongs to the space group C_{6v}^4 in the Schoenflies notation and $P6_3mc$ in the Hermann–Mauguin notation. A schematic representation of the wurtzitic ZnO structure is shown in Figure 1.2. The structure is composed of two interpenetrating hexagonal close-packed (hcp) sublattices, each of which consists of one type of atom displaced with respect to each other along the threefold c-axis by the amount of $u = 3/8 = 0.375$ (in an ideal wurtzite structure) in fractional coordinates. The internal parameter u is defined as the length of the bond parallel to the c-axis (anion–cation bond length or the

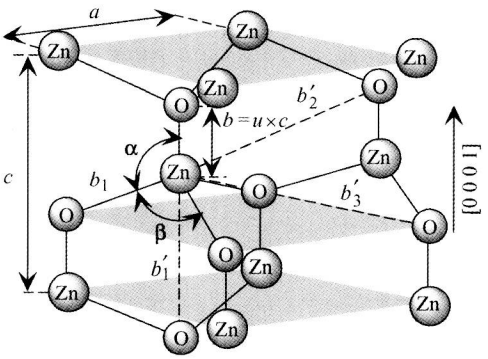


Figure 1.2 Schematic representation of a wurtzitic ZnO structure with lattice constants a in the basal plane and c in the basal direction, u parameter, which is expressed as the bond length or the nearest-neighbor distance b divided by c (0.375 in ideal crystal), α and β (109.47° in ideal crystal) bond angles, and three types of second-nearest-neighbor distances b'_1, b'_2, and b'_3.

nearest-neighbor distance) divided by the c lattice parameter. The basal plane lattice parameter (the edge length of the basal plane hexagon) is universally depicted by a; the axial lattice parameter (unit cell height), perpendicular to the basal plane, is universally described by c. Each sublattice includes four atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron. The crystallographic vectors of wurtzite are $\vec{a} = a(1/2, \sqrt{3}/2, 0), \vec{b} = a(1/2, -\sqrt{3}/2, 0)$, and $\vec{c} = a(0, 0, c/a)$. In Cartesian coordinates, the basis atoms are (0, 0, 0), (0, 0, uc), $a(1/2, \sqrt{3}/6, c/2a)$, and $a(1/2, \sqrt{3}/6, [u+1/2]c/a)$.

In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio or the u value. The experimentally observed c/a ratios are smaller than ideal, as in the case of GaN, where it has been postulated that not being so would lead to zinc blende phase [1]. It should be pointed out that a strong correlation exists between the c/a ratio and the u parameter in that when the c/a ratio decreases, the u parameter increases in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to long-range polar interactions. These two slightly different bond lengths will be equal if the following relation holds:

$$u = \left(\frac{1}{3}\right)\left(\frac{a^2}{c^2}\right) + \frac{1}{4}. \tag{1.1}$$

The nearest-neighbor bond lengths along the c-direction (expressed as b) and off c-axis (expressed as b_1) can be calculated as

$$b = cu \quad \text{and} \quad b_1 = \sqrt{\frac{1}{3}a^2 + \left(\frac{1}{2} - u\right)^2 c^2}. \tag{1.2}$$

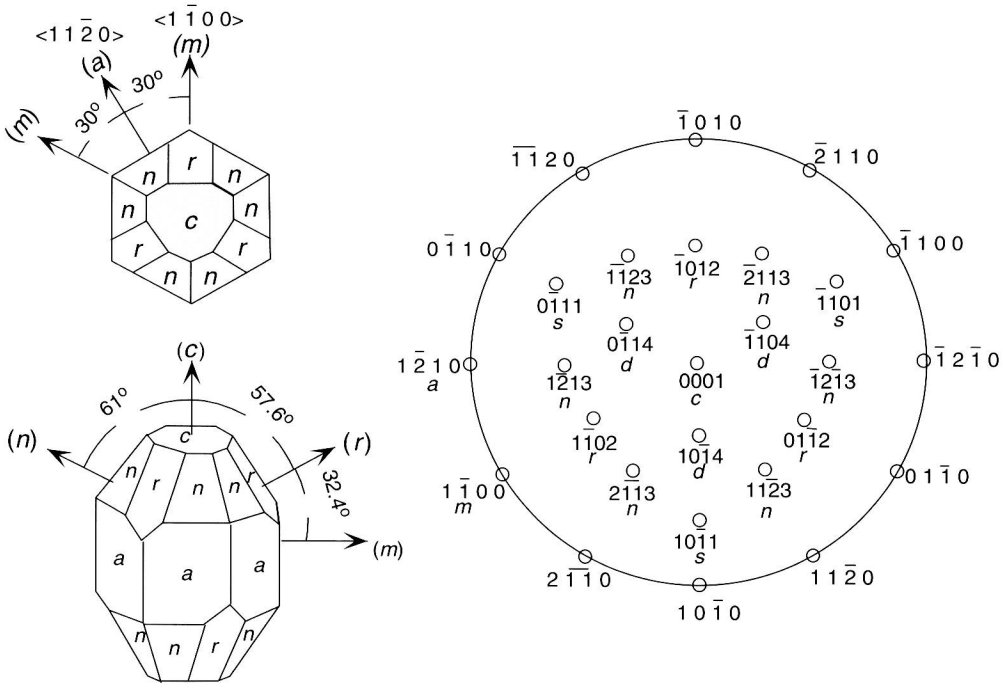
In addition to the nearest neighbors, there are three types of second-nearest neighbors designated as b'_1 (one along the c-direction), b'_2 (six of them), and b'_3 (three of them) with the bond lengths [2]

$$b'_1 = c(1-u), \quad b'_2 = \sqrt{a^2 + (uc)^2}, \quad \text{and} \quad b'_3 = \sqrt{\frac{4}{3}a^2 + c^2\left(\frac{1}{2} - u\right)^2}. \tag{1.3}$$

The bond angles, α and β, are given by [2]

$$\begin{aligned} \alpha &= \pi/2 + \arccos\left[\left(\sqrt{1 + 3(c/a)^2(-u+1/2)^2}\right)^{-1}\right], \\ \beta &= 2\arcsin\left[\left(\sqrt{4/3 + 4(c/a)^2(-u+1/2)^2}\right)^{-1}\right]. \end{aligned} \tag{1.4}$$

The lattice parameters are commonly measured at room temperature by X-ray diffraction (XRD), which happens to be the most accurate one, using the Bragg law. In ternary compounds, the technique is also used for determining the composition;



Common crystallographic planes in sapphire

Plane name	Miller index	d spacing
a	(11$\bar{2}$0)	2.379 Å
m	(10$\bar{1}$0)	1.375 Å
c	(0001)	2.165 Å
r	(1$\bar{1}$02)	1.740 Å
n	(11$\bar{2}$3)	1.147 Å
s	(10$\bar{1}$1)	1.961 Å

Angles between common planes

(0001) ^ (1$\bar{1}$02)	c ^ r	57° 35′
(0001) ^ (11$\bar{2}$3)	c ^ n	61° 11′
(0001) ^ (10$\bar{1}$1)	c ^ s	72° 23′
(0001) ^ (11$\bar{2}$1)	c ^	79° 37′
(0001) ^ (11$\bar{2}$0)	c ^ a	90° 00′
(0001) ^ (10$\bar{1}$0)	c ^ m	90° 00′
(11$\bar{2}$0) ^ (10$\bar{1}$0)	c ^ m	30° 00′

Figure 1.3 Labeling of planes in hexagonal symmetry (for sapphire).

however, strain and relevant issues must be taken into consideration as the samples are in the form of epitaxial layers on foreign substrates. The accuracy of the X-ray diffraction and less than accurate knowledge of elastic parameters together allow determination of the composition to only within about 1% molar fraction. In addition to composition, the lattice parameter can be affected by free charge, impurities, stress, and temperature [3]. Because the c/a ratio also correlates with the difference of the electronegativities of the two constituents, components with the greatest differences show largest departure from the ideal c/a ratio [4].

The nomenclature for various commonly used planes of hexagonal semiconductors in two- and three-dimensional versions is presented in Figures 1.3 and 1.4. The Wz ZnO lacks an inversion plane perpendicular to the c-axis; thus, surfaces have either a group II element (Zn, Cd, or Mg) polarity (referred to as Zn polarity) with a

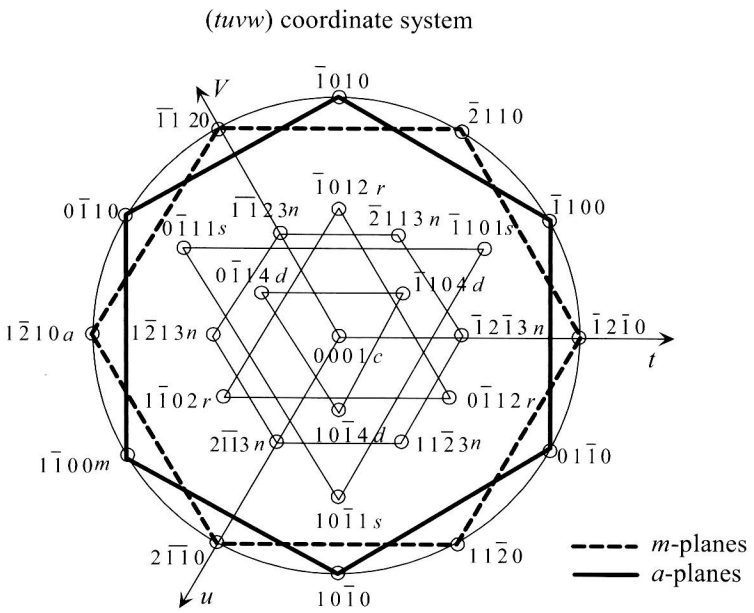


Figure 1.4 A magnified view of labeling of planes in hexagonal symmetry in the (*tuvw*) coordinate system with *w* representing the unit vector in the *c*-direction. The lines simply show the symmetry only. If the lines connecting *m*-points among each other and *a*-points among each other were to be interpreted as the projection of those planes on the *c*-plane, the roles would be switched in that the lines connecting the *m*-points would actually represent the *a*-planes and lines connecting the *a*-points would actually represent the *m*-planes, which are normal to the plane of the page.

designation of (0 0 0 1) or (0 0 0 1)*A* plane or an O polarity with a designation of $(0\,0\,0\,\bar{1})$ or $(0\,0\,0\,\bar{1})B$ plane. The distinction between these two directions is essential due to polarization charge. Three surfaces and directions are of special importance, which are (0 0 0 1), $(1\,1\,\bar{2}\,0)$, and $(1\,\bar{1}\,0\,0)$ planes and the directions associated with them, $\langle 0\,0\,0\,1\rangle$, $\langle 1\,1\,\bar{2}\,0\rangle$, and $\langle 1\,\bar{1}\,0\,0\rangle$, as shown in Figure 1.5. The (0 0 0 1), or the basal plane, is the most commonly used surface for growth. The other two are important in that they represent the primary directions employed in reflection high-energy electron diffraction (RHEED) observations in MBE growth, apart from being perpendicular to one another.

The *zinc blende* ZnO structure is metastable and can be stabilized only by heteroepitaxial growth on cubic substrates, such as ZnS [5], GaAs/ZnS [6], and $Pt/Ti/SiO_2/Si$ [7], reflecting topological compatibility to overcome the intrinsic tendency of forming wurtzite phase. In the case of highly mismatched substrates, there is usually a certain amount of zinc blende phase of ZnO separated by crystallographic defects from the wurtzite phase. The symmetry of the zinc blende structure is given by space group $F\,43m$ in the Hermann–Mauguin notation and T_d^2 in the Schoenflies notation and is composed of two interpenetrating face-centered cubic (fcc) sublattices shifted along the body diagonal by one-quarter of the length of