PREFACE

Compound semiconductor materials are becoming more important year by year as the basic materials for electronic and optical applications. It has already become clear that Si is the most indispensable material for the present prosperity in the electronic and information/communication industry. It is used in ICs for computers which are the main products in the present electronic industry. The silicon industry is now extensively developed in many fields mainly for micro processing units (MPUs) and memories for computers and for power devices for switching power supplies and for control units for hybrid automobiles.

Compound semiconductors are attractive since they have different properties from those of elementary semiconductors such as Si and Ge. Because of their possibilities, much research has been devoted to developing these compound semiconductors such as III-V materials, II-VI materials, IV-IV materials, nitrides, SiC, chalcopyrite and other materials. In order to realize various applications using these materials, it is indispensable to grow high quality single crystals.

Main applications of compound semiconductors are infrared and visible LEDs based on the photoemission characteristics. For these applications, conductive GaP and GaAs substrates are industrially produced and widely used. GaAs substrates are also used for infrared and visible light LDs. GaP is mainly grown by the LEC method and conductive GaAs is mainly grown by horizontal boat methods. High quality GaAs crystals have been recently grown by the VB/VGF methods. Conductive GaP and GaAs for LEDs and LDs have become a big market and have led the compound semiconductor industry.

Semi-insulating (SI) GaAs has been developed worldwide in the 80's in the expectation that it would find application in high speed super-computers. In fact, GaAs electronic device and ICs have been extensively explored for application in the high frequency field exceeding 10 GHz. SI-GaAs however could not find its application in this field. This was because large computers can be water-cooled so that silicon devices could compete with GaAs. The main application of GaAs was HEMTs for satellite broadcasting where high frequency devices of 10 GHz were required, but its take-up was less than expected for computer applications. In this period, many manufacturers have been disappointed and it seemed that no large application can be found for SI-GaAs.

The turning point for SI-GaAs was for cellular phones which need low power consumption devices at high frequency but only at 800 MHz, which was much less than people expected for GaAs. When this application was required, the GaAs technology community could react quickly since the technology was already matured for higher level computer applications. The production of GaAs devices started simultaneously with the rise of the cellular phone business. Because of this unexpected success, SI-GaAs became the third main industrial material.

Another application of compound semiconductors is InP based optical devices, laser and detectors for quartz fiber communications. The development of an information society based on the Internet accelerated the development of InP materials and devices. The development of InP started early in the 70's and it was a long time before the FTTH (fiber to the home) system was recently networked in individual homes.

Other III-V materials such as InAs, InSb, GaSb do not have the applications for a large market. They can be used as far infrared detectors, Hall sensors, but the consumption is still small compared with others. They however have other potentialities as high frequency devices and thermovoltaic devices.

Applications are rather difficult to find for II-VI materials because of the difficulty in crystal growth and conductivity type control because of the specific self-compensation problem. Industrially, polycrystalline ZnSe is used as window material for high power lasers and CdTe is used as substrate for far-infrared detectors in the wavelength range of 10 μm. The development of ZnSe was prominent and short wavelength LDs and LEDs have actually been made. Technologically, the application of ZnSe was nearly ready for the real industrialization but was in vain because of the quick development of GaN LDs and LEDs. This however does not deny the future challenging possibility of ZnSe.

Other II-VI materials such as CdS, CdSe, ZnS and ZnTe have long been studied but except the application of CdS for photodetectors, important applications have not yet been found.

As new materials, GaN based epitaxial layers are now important for shortwave length LEDs and LDs. These epitaxial layers are firstly grown on sapphire substrates, but SiC has been developed as a substrate for these applications. Since there is a large lattice mismatching for these devices, GaN substrates are strongly desired and various crystal growth methods are now under investigation. SiC crystal growth was mainly developed for its application as substrate for GaN epitaxial growth, but SiC crystal itself is now widely desired for power devices, mainly for automobile and switching applications.

For growing these compound semiconductor crystals, a variety of methods have been studied and developed. In the early days, melt growth methods such as horizontal boat methods (HB/HGF/HZM methods) and the liquid encapsulated Czochralski (LEC) method were predominant. Vertical boat growth methods (VB/VGF methods) which were not applied for a long period for industrial production have however been reconsidered and are now going to reach the stage of industrial production. Not only melt growth methods but also vapor phase growth methods is becoming more widely used in industry. New methods of crystal growth are still being developed and each in turn can be considered as the new method. In this sense, the crystal growth method is not yet fully established and there is always a possibility of new methods to replace the present one. For this to happen, the new method has to be able to have better cost performance with the ability to grow better quality crystals. The reader may find some clue for this new method in the various past trials described in this book.

In this way, several compound semiconductors have found industrial applications and in fact they are industrially produced. The scale of total material production in the world now exceeds 900 million dollars and is steadily increasing. It is therefore clear that the field of compound semiconductors will become a large business, which has come after Si by compensating for what Si can not do, such as light emitting, high-power and high-frequency devices. The above market scale is only for bulk and epitaxial materials. It should be noted that the market scale of devices using these compound semiconductors is at least ten times more, and that of final systems are at least one hundred times more than that of materials. This means that these compound semiconductor materials support and contribute to the market scale of 90 billion dollars as a new industry.

It however should be noted that this increasing prosperity of compound semiconductors did not arise suddenly in a short period of research and development. In fact, the study of most of them started more than 50 years ago. Many researchers devoted most of their lives in research and development of compound semiconductor materials, by dreaming and believing in the realization of useful devices based on these materials even at the time when there was no evidence and proof for their future success. And finally, we are now convinced that their belief was true and the existence of these materials has proved of value in this society. We should not forget the efforts of these pioneering scientists and engineers. This success could not be achieved without their convinced belief and effort.

In this book, I summarize and update most of their fundamental work in a way that young students, engineers and scientists can be in touch with how these materials have been developed against what kind of obstacles and how they were overcome, and what are even now to be overcome. I have tried to construct this book in such a way that everybody will be able to grasp the essence of bulk compound semiconductor materials as quickly as possible.

For this purpose, in Part 1, fundamentals are written in such a way that the basics will be covered without special knowledge. In Part 1, physical properties, bulk crystal growth methods, principles of bulk crystal growth, defects, characterization methods and applications are covered. Those who are familiar with these subjects can skip Part 1 depending on their knowledge. Part 1 however can be used as a reference to the terminology which appears in Part 2 and 3 where each compound semiconductor material is discussed in detail. In Part 2, III-V compound semiconductors and in Part 3, II-VI compound semiconductors are reviewed. In each chapter, as many references as possible are reviewed so that all efforts in each material are covered. I hope that this book will help the further development of compound semiconductor materials not only in developed countries but also in others which are developing rapidly.

This book took a long time to write because I was engaged in a company affiliation for the research and development and most of my time was spent on practical industrial development. I however believe that the experience in industry will help me to arrange the book's content, focusing on the real priorities in the development of bulk compound semiconductor materials. I would like to thank very much everyone in Japan Energy Corporation where the author spent twenty years in the field of bulk crystal growth and characterization activities. I am especially grateful to ex-directors T. Ogawa, I. Tsuboya, Y. Koga, K. Aiki, I. Kyono and T. Ohtake for their encouragement and useful discussion and Drs. K. Hirata, A. Onozuka, K. Kainosho, R. Hirano, K. Sato, S. Asahi and M. Uchida and Messrs T. Fukui, K. Katagiri, T. Fukui, M. Ohoka, D. Kusumi, H. Yamamoto, M. Seiwa, M. Oyake, H. Sawatari, S. Katsura, K. Matsumoto, H. Okazaki, K. Kohiro, T. Inoue, G. Kano, Y. Seki, M. Mori, H. Shimakura, H. Momoi, K. Urata, S. Yaegashi, T. Imaizumi, A. Noda, A. Arakawa, M. Ohta and Ms. Y. Matsuda for their collaboration, and Drs. M. Ohmori, H. Araki, J. Takahashi, K. Suga, U. Nakata, H. Kurita, M. Taniguchi, Y. Taniguchi for the helpful discussions I had with them. I would like to express my appreciation for all scientists who made helpful suggestions and with whom I had good discussions in a kindhearted manner with a warm friendship. They are Professors G. Müller at University Erlangen-Nüernberg, D.C. Look at Wright State University, P. Rudolph at IKZ (Institut für Kristallzuchtung), S. Porowski at High Pressure Research Center, B.H.T. Chai at University of Central Florida, H.J. Scheel at Ecole Polytechnique Federal Lausanne, S. Nakamura at University of California, T. Fukuda, M. Isshiki, T. Yao and S. Uda at Tokoku University, T. Ogawa at Gakushuin University, M. Umeno at Chubu University, T. Sasaki and H. Asahi at Osaka University, H. Hasegawa at Hokkaido University, F. Hasegawa at Tsukuba University, T. Egawa at Nagoya Instutut of Technology, T. Taguchi and K. Tadatomo at Yamaguchi University, M. Tajima at Institute Space Astron. Sci., Y. Nanishi at Ritsumeikan University, A. Yoshikawa at Chiba University, A. Yoshida and A. Wakahara at Toyohashi University, K. Hiramatsu at Mie University, M. Kasuga and T. Matsumoto at Yamanashi University, K. Kishino at Sophia University, M. Yamada at Kyoto Institute of Technology, O. Wada at Kobe University, K. Terashima at Shonan Institute of Technology and Drs. D.J. Stirland and M.R. Brozel at GEC Marconi, C.J. Miner at Bell-Northern Research, R. Fornari at MASPEC, D. Bliss at AFRL/Hanscom AFB, V. D. Mattera at ATT Bell Lab. R. Triboulet at CNRS Meudon, E. Molva and B. Daudin at Centre de l'Energie Nucleaires de Grenoble, G. Jacob at Inpact, J.P. Faurie at Lumilog, M. Huber at Thomson-CSF, J.H. Maurice at AFOSR/AFOARD, S. Watanabe at Lumiled, K. Matsumoto at Taiyo Nippon Sanso, A. Ishibashi and N. Nakayama at Sony, M. Abe at Hoya Advanced Semiconductor Technology, T. Sekiguchi at NRIM, U. Makita and Y. Sugiyama, K. Arai, H. Okumura at Electrotechnical Lab. (presently AIST), S. Miyazawa at NTT (presently Waseda University), K. Hoshikawa at NTT (Presently Shinshu University), S. Shinoyama at NTT (presently NEL Crystal), K. Itoh at NEC, D. Ueda and U. Ban at Matsushita Electric Industries, K. Moriya at Mitsui Mining & Smelting, N. Ohtani at Nippon Steel, M. Isemura and M. Hata at Sumitomo Chemical, K. Uehara at Kobe Steel, R. Ohno at Acrorad and M. Tanaka and M. Imaeda at NGK Insulators. I also would like to thank very much for those with whom I was able to have fruitful discussions during JAMS and SEMI activities for compound semiconductor material standardization. They are S. Okubo, M. Kashiwa, Y. Otoki, S. Kuma at Hitachi Cable, K. Ushio, T. Kikuta, J. Kikawa, Y. Ito and S. Yoshida at Furukawa Electrics, Y. Kadota, A. Tanaka and Y. Masa at Sumitomo Metal Mining, Y. Sano at Oki Electric Industry, K. Yamada and T. Takahashi at Shin-Etsu Semiconductors, T. Sato at Showa Denko, K. Fujita and M. Tatsumi at Sumitomo Electric Industries, H. Goto, M. Kitsunai and Y. Katsuno at Mitsubishi Chemicals, R. Toba, K. Iwasaki and N. Narita at Dowa Mining and K. Kashima at Toshiba Ceramics.

I want to acknowledge Dr. F.S. Skeffington for his careful and thorough review of the manuscript and Ms. M. Ng at World Scientific Corporation for awaiting with patience the completion of this book, and understanding its value. Finally, I wish especially to thank my wife Mikiko and my daughter Tomoko for their encouragement during the writing of this book.

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Nagoya, Japan
October 2006