Physics and Properties of Narrow Gap Semiconductors

MICRODEVICES

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Preface

The physics of narrow-gap semiconductors is an important branch of semiconductor science. Research into this branch focuses on a specific category of semiconductor materials which have narrow forbidden band gaps. Past studies on this specific category of semiconductor materials have revealed not only general physical principles applicable to all semiconductor technology, but also those unique characteristics originating from the narrow band gaps, and therefore have significantly contributed to science and technology. Historically, developments of narrow-gap semiconductor physics have been closely related to the development of the science and technology of infrared optical electronics as narrow-gap semiconductors have played a vital role in the field of infrared-radiation detectors and emitters, and other high speed devices. The present book is dedicated to the study of narrow-gap semiconductors and their applications. It is expected that the present first volume will be valuable to not only the fundamental science of narrow-gap semiconductors but also to the technology of infrared optical electronics.

There have been several books published in this field over the past few decades. In 1977, a British scientist, D.R. Lovett, published a book *Semimetals and Narrow-Band Gap Semiconductors* (Pion Limited, London). Later, German scientists, R. Dornhaus and G. Nimtz, published a comprehensive review article in 1978, whose second edition, entitled, *The Properties and Applications of the HgCdTe Alloy System, in Narrow Gap Semiconductors*, was reprinted by Springer in 1983 (Springer Tracts in Modern Physics, Vol. 98, p. 119). These two documents included systematic discussions of the physical properties of narrow-gap semiconductors and are still important references of the field. In 1980, the 18th volume of the series *Semiconductors and Semimetals* (edited by R.K. Willardson and Albert C. Beer) in which very useful reviews were collected, was dedicated to HgCdTe semiconductor alloys and devices. In 1991, a Chinese scientist, Prof. D.Y. Tang published an important article, "Infrared Detectors of Narrow Gap Semiconductors" in the book *Research and Progress of Semiconductor Devices* (edited by S.W. Wang, Science Publish, Beijing, pp. 1–107), in which the fundamental principles driving HgCdTe-based infrared radiation detector technology were comprehensively discussed. In

addition, a handbook, *Properties of Narrow Gap Cadmium-Based Compounds* (edited by P. Capper), was published in the United Kingdom in 1994. In this handbook, a number of research articles about the physical and the chemical properties of HgCdTe narrow-gap semiconductors were collected and various data and references about Cd-based semiconductors can be found.

This book *Narrow Gap Semiconductors* is being divided into two volumes. The first volume is subtitled *(Vol. I): Materials Physics and Fundamental Properties*. The second volume subtitled, *(Vol. II): Devices and Low-Dimensional Physics*, will follow. Volume II will have the following table of contents:

The present book (*Narrow Gap Semiconductors: (Vol. I): Materials Physics and Fundamental Properties*) and the forthcoming book (*Narrow Gap Semiconductors (Vol. II): Devices and Low-Dimensional Physics*) aim, in the two volumes, at characterizing a variety of narrow-gap semi-conductor materials and revealing the intrinsic physical principles that govern their behavior. The discussions dedicated to narrow-gap semiconductors presented in this book evolved within the larger framework of semicon-ductor physics, in combination with the progresses in the specific field of narrow-gap semiconductor materials and devices. In particular, a unique property of this book is the more extensive collection of results than ever previously assembled of the research results deduced by Chinese scientists, including one author of this book. These results are integrated into the larger body of knowledge from the world literature. In organizing the book, special attention was paid to bridging the gap between basic physical principles and frontier research. This is achieved through extensive discussions of various aspects of the frontier theoretical and experimental scientific issues and connecting them to device related technology. It is expected that both the students and the researchers working in relevant fields will benefit from this book.

The book was encouraged and advised by Prof. D.Y. Tang. One of the authors (J. Chu) is most grateful to Prof. D.Y. Tang's critical reading of the manuscript and invaluable suggestions and comments. The co-author (A. Sher) is indebted to Prof. A.-B. Chen for invaluable suggestions. The authors are also grateful to numerous students and colleagues who over the years have offered valuable support during the writing of this book. They are Drs.: Y. Chang, B. Li, Y.S. Gui, X.C. Zhang, S.L. Wang, Z.M. Huang, J. Shao, X. Lu, Y. Cai, K. Liu, L. He, M.A. Berding, and S. Krishnamurthy. We are indebted to Professor M.W. Muller for his careful

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Contents

1 Introduction

Narrow gap semiconductors are members of the semiconductor family with narrow forbidden fundamental bands. Generally materials with forbidden bandwidth E_g smaller than 0.5 eV, or equivalently those with forbidden bandwidth corresponding to an infrared absorption cut-off wavelength over 2 μm, are taken as narrow gap semiconductors (Long and Schmit 1973; Dingyuan Tang 1976).

1.1 Narrow Gap Semiconductors

Characteristics of the energy bands of narrow gap materials include strongly non-parabolic conduction bands, and spin–orbit splittings even larger than the fundamental band gaps. The early energy band electronic structures of the narrow gap semiconductors were based on a model theory of the InSb semiconductor put forward by Kane in 1957 (Kane 1957, 1966). While this theory properly predicted tends, it was not sufficiently accurate to serve as a reliable engineering tool. Newer theories based on "density functional theory," or the simpler "hybrid psudopotential-tight-binding theory (HPTB)" (Chen and Sher 1995), now are sufficiently accurate for such use.

HgCdTe alloys and InSb are the typical narrow gap semiconductor materials. In intrinsic infrared detectors, radiation excites electrons in states near the top of the valence band of the narrow gap semiconductor to electron states near the bottom of the conduction band. This results in non-equilibrium electron–hole populations, which change the electrical transport properties of the material. In photoconductive devices, the conductivity increases, whereas in photovoltaic devices, a photo-voltage is generated in response to the incident photon flux. With their small effective electron masses, high electron mobility, and long carrier lifetimes, these narrow gap semiconductors are sensitive and fast infrared photo detector materials, suitable for both infrared scene sensing and high data rate communication applications (Kane 1981). Thus the development of narrow gap semi-conductor physics is closely related to infrared detector applications.

Infrared detectors are the core components of modern infrared imaging systems and the demand for and development of infrared detectors for high performance systems has promoted the fabrication of improved narrow gap semiconductors and driven their physics research.

The development of narrow gap semiconductor physics has experienced three stages. The first stage started from the 1940s when PbS, PbSe and PbTe detectors were the main infrared detector materials. The 1950s saw the first use of InSb, InAs and Hg doped Ge (Ge:Hg) materials. Experimentally, advances were made in the preparation and research on the properties of InSb. Theoretically clear and definite results were also derived from research on the properties of Ge and Si energy band structures. Based on this group IV material work, E. O. Kane calculated, by adding **$k \cdot P$** perturbation theory to the model, the InSb energy bands. His work pioneered the understanding of the mechanisms responsible for the energy bands of narrow gap semiconductors. The theory well describes the observed trends in the relationship between energy bands and wave vectors, the dispersion of InSb near the Γ-point of the k-space Brillouin zone. It serves as the basis for describing various processes, such as carrier transport and photo-electronic excitation, etc. Consequently it laid the theoretical foundation for the research of narrow gap semiconductor physics. This period was marked mainly by the establishment of narrow gap semiconductor energy band theory.

The second period began in the 1960s, during which a comprehensive investigation was devoted to finding the best narrow gap semiconductor materials for different system applications. Prior to ~1960 people adopted infrared detectors prepared by using PbS, InSb and Ge:Hg (Ge doped with Hg), that were applied in the three "transparent atmospheric windows" with wavelength bands at 1–3 μm (short-wave infrared or SWIR), 3–5 μm (mid-wave or MWIR), and 8–14 μm (long-wave or LWIR), respectively.

According to the spectral distribution rule for blackbody radiation, the thermal radiation of room temperature objects is distributed mainly in the 8–14 μm bands. InSb has a long wavelength cut-off near 5 μm, so its detection efficiency (responsivity) to the radiation emitted by a room temperature object is relatively low. Ge:Hg heavily impurity doped photo-conductive detectors operating in the range of 8–14 μm are suitable for thermal imaging of room temperature objects. However, they only work well when operated at temperatures below ~40 K, which is inconvenient for many practical applications. Moreover, its cut-off wavelength is not optimum. Therefore, people searched for intrinsic photoconductive or photovoltaic detector materials operating at higher temperature while still

being responsive in the 8–14 µm range. In order to obtain the best response in the 8–14 µm atmosphere window the detector material must be a semiconductor with its forbidden bandwidth around 0.09 eV. However, there are no elemental semiconductors, or binary compound semi-conductors with such forbidden bandwidths. Hence, it was necessary to fabricate an artificially synthesized alloy semiconductor by adjusting the alloy composition to make its forbidden bandwidth about 0.1 eV. The $Hg_{1-x}Cd_xTe$ semiconductor alloy with Cd concentration x, is such an ideal intrinsic infrared radiation detecting material. HgCdTe can be considered a pseudo-binary semiconductor of (HgTe) and (CdTe). Figure 1.1 shows the relationship between the forbidden bandwidth E_g and lattice constant a of some compound semiconductor materials. It can be seen from the figure that the II–VI semimetal compound HgTe ($E_g = -0.3$ eV), and the wide forbidden band semiconductor CdTe ($E_g = 1.6$ eV) both with zinc-blende structures, have lattice constants that are very close, $\Delta a/a = 0.3\%$. This enables HgTe, and CdTe to form continuous solid solutions of $(HgTe)_{1-x}(CdTe)_x$ pseudo binary alloy systems at various concentration ratios x. By varying the concentration of Cd, the alloy can have semimetal behavior like HgTe or semiconductor behavior like CdTe. Since $E_g = E(\Gamma 6) - E(\Gamma 8)$, at 4.2 K, E_g is –0.3 eV when $x = 0$ and 1.6 eV when $x = 1$ (Chen and Sher 1995). The bandwidth varies nearly linearly with x having only a slight bowing between –0.3 and 1.6 eV. At 4.2 K, when the composition $x = 0.161$, $E_g = 0$. Since the band gap of $Hg_{1-x}Cd_xTe$ varies continuously with composition x, this enables it to cover the entire infrared wave band, so it is an important material for preparing infrared detectors. This type of materials can be used not only to replace Ge:Hg for preparing detectors with response wavelength in the range of 8–14 µm with the added advantage of operating at 77 K, but also to substitute for PbS and InSb detectors working at room temperature in the ranges of 1–3 µm and 3–5 µm. By proper composition adjustments this material can also be applied to make PIN-type avalanche photo-diode detectors operating at 1.3 and 1.55 µm for application in optic-fiber communication. This alloy can cover the whole spectral range of 1–30 µm (Long and Schmit 1973; Stelzer et al. 1969).

Besides its many detector applications, this alloy system has proved to be a valuable aid to address fundamental research questions. Because its band gap can be adjusted by changing the composition, it has enabled detailed studies of the band gap variation of transport processes, optical properties, magneto-optic effect, lattice vibration characteristics, etc.
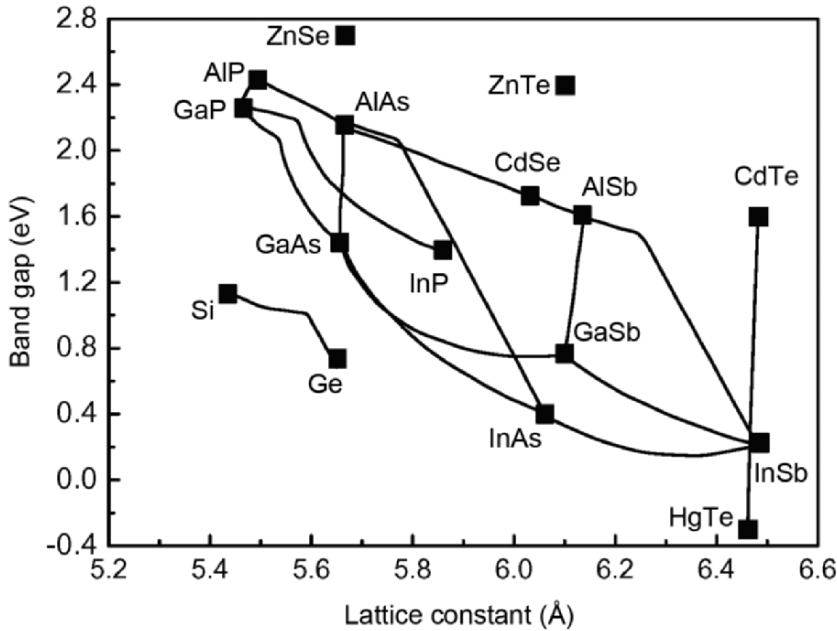
Fig. 1.1. Energy band gap versus lattice constant for semiconductor compounds

In 1959 Lawson and his collaborators first published their research results on HgCdTe (Lawson 1959). Because of the initial difficulty of preparing the material, however, it was not till 1970s, when there was progress of crystal growth capabilities by means of melting and epitaxial techniques, that significant advances on physics research of HgCdTe materials and device fabrication began. In China, Dingyuan Tang initiated in 1967 comprehensive investigations of HgCdTe materials and devices (Dingyuan Tang 1976, 1974). Starting in 1982 the major advances in HgCdTe research were captured in the proceedings of meetings initially entitled "The U.S. Workshop on the Physics and Chemistry of Mercury Cadmium Telluride." In 1992 the meeting's title was changed to add "Other IR Materials," and still later in 1996 it was changed again to become "The U.S. Workshop on the Physics and Chemistry of II–VI Materials." While the term "U.S." appears in the title, in fact it has always been an international meeting.

In the late 1980s HgCdTe materials were applied in the research and development of single-element, multi-element, linear array and two-dimensional focal plane array infrared detector systems. The developments in this period verified that HgCdTe is a relatively ideal infrared detecting material (Long and Schmit 1973). It is a direct band gap semiconductor, so

infrared detectors prepared with it are intrinsic. Its corresponding optical process involves a transition between energy band states, which avoids the fundamental disadvantages of impurity-type infrared detectors.

In summary, the main advantages of employing HgCdTe material for preparing infrared detectors are:

– The forbidden bandwidth can be adjusted to cover the entire infrared wave band.
– The material has a large photo-absorption coefficient which enables the inner quantum efficiency generated in a device with a thickness of only 10–15 μm to approach 100%.
– The electron and hole mobilities are high.
– The intrinsic mechanism generates long-lived carriers and a relatively low thermal generation rate, which enables devices to operate at higher temperature.
– There is a good lattice match between CdTe and HgTe, which allows preparation of high quality epitaxial heterostructures on large CdTe substrates.
– The residual impurity concentration can be as low as 10^{14} cm^{-3}.
– It can be doped to make it p-type or n-type.
– Its surface can be passivated.

HgCdTe, however, also has some disadvantages, such as:

– The Hg–Cd bond is weak and at growth temperature Hg vacancies appear if proper controls are not exercised.
– The Hg vacancy is an acceptor, but it also degrades carrier lifetimes so it is not an optimum dopant.
– On a Te site, As is an acceptor, but on a Hg site it is a donor, and it requires stringent growth controls to get it properly positioned.
– Precipitation of Te is also a serious problem.

To realize practical device performance it has been necessary to solve these and other related problems in dopants, point and extended defects, compositional uniformity, etc. In an effort to overcome these materials problems, workers in the field began to adopt epitaxial growth techniques, in addition to conventional bulk crystal growth. HgCdTe based detector systems were advertised by French groups as early as 1967, and by the end of the 1970s the first generation of single-element HgCdTe infrared detectors became mature (Chapman 1979). In 1980s the second generation linear array detectors and small-scale area array detectors (Elliot 1981) were fabricated. Later the third generation of LWIR linear arrays and large-scale focal plane area arrays were successfully developed (Arias et al. 1989). An essential aspect of the ability to grow suitable epitaxial

material was the development of large areas of Bridgman technique bulk grown CdZnTe substrate crystals lattice matched to the active HgCdTe devices (Harman 1980; Arias et al. 1993). In order to realize monolithic integration with read out chips, efforts were made to use Si and GaAs crystals as substrates, but their large lattice mismatch to the epitaxial HgCdTe introduced high densities of mismatch and treading dislocations that degrade device performance relative to that achieved on lattice matched CdZnTe substrates (Brill et al. 2001; Varesi et al. 2001). In this period, systematic progress on narrow gap semiconductors was made; on their growth, characterization methods, physics research, and device structures (Dornhaus and Nimtz 1983; Lovett 1977; Dingyuan Tang and Feimin Tong 1991).

The third stage of the development on narrow gap semiconductor physics started in the 1990s. In this stage more and more importance was attached to the research of HgCdTe thin film materials, and to the third generation long linear array and large scale focal plane area array based systems. The study of narrow gap semiconductor physics went deeper and deeper. The quality of HgCdTe thin film materials prepared by means of liquid phase epitaxy (LPE) (Schmit and Bowers 1979), metal-organic chemical vapor deposition (MOCVD) (Irvine and Mullin 1981) and molecular beam epitaxy (MBE) (Faurie et al. 1982) in addition to the bulk material growth methods (Micklethwaite 1981) made substantial advances. The growth techniques were successfully applied in making infrared focal plane arrays. Materials specifications for MWIR devices are more forgiving than those for LWIR devices. The fabrication rules for MWIR applications were refined and those for LWIR were brought to a level capable of supporting practical systems. This involved establishment of greatly improved composition control, electrical parameter control and doping control for large area thin films. In this process the links between material growth, physical characterization, device design, and device fabrication became ever closer. For example it inspired the use of hetero-junctions rather than simple p–n homojunctions: because heterojunctions could be fabricated by epitaxial growth methods. In addition to improving materials features previously mentioned, people now studied the impact on thin films of ion beam etching; this process not only modifies surface impurity states, but can also propagate impurities into existing p–n junctions. The impact of long-term exposure to light on the material and consequent device degradation were determined. Details of the spatial structure of the p–n hetero-junction electrical characteristics and its photoelectric response were extensively modeled, and practical device designs were devised taking advantage of the improved knowledge base. There were also investigations of the band structures at surfaces where

two-dimensional electron gases can form to degrade device passivation. On the basis of these studies the technical device specifications were further perfected for the preparation of narrow gap semiconductor infrared focal plane arrays. At present, 512×512 and $1,024 \times 1,024$ element large scale HgCdTe infrared focal plane arrays have been built successfully. At the same time, people are making efforts to explore the new effects of photoelectric conversion, electro-optical conversion and opto-optic conversion and their new applications in infrared focal plane arrays and new types of photoelectric devices (Levine 1993; Levine et al. 1987; Choi and Eglash 1992; Choi and Turner 2000).

Advances of the general semiconductor discipline spilled over into new research ideas for producing narrow gap semiconductors. Many of these centered on research into the photoelectric conversion process in microstructures: superlattices, quantum wires, quantum wells, and quantum dots. Others looked into the advantages that could be derived from sub-band structures of bulk material. Spin electron states were studied in low-dimensional structures along with their optical transition, tunneling and transport rules, in strong magnetic fields and at ultra low temperatures. The research into characterization methods applied to semiconductors involved several optical and electrical experimental means, including infrared fluorescence spectroscopy, infrared magneto-optics spectroscopy, infrared elliptic polarization spectroscopy, micro-regional spectroscopy, flat band capacitance spectroscopy, and quantitative mobility spectroscopy. Additionally, older methods for measuring transport characteristics were extended to ultra-low temperatures and high magnetic fields.

Investigation of narrow gap semiconductors has evolved rapidly as a result of the development of the general semiconductor discipline, and of the ever more stringent requirements placed on infrared devices over the past decade. People continuously discover new phenomena from their investigations, enriching the knowledge base of the semiconductor discipline. Semiconductor science development, at the same time, is closely related with infrared optics and photo-electronic science and with technology, and their applications (including applications in the fields of aeronautical and space infrared remote sensing of the earth environment, military applications, and various ground based civil engineering applications. The accumulation of the research work has spawned the formation of a new discipline; "narrow gap semiconductor physics," with HgCdTe as one of its principal objects.

In addition to HgCdTe and InSb, narrow gap semiconductors also include α-Sn, HgSe, HgCdSe, HgSe, HgCdSe, HgS_xSe_{1-x}, $Hg_{1-x}Mn_xTe$, $Hg_{1-x}Zn_xTe$, PbS, PbSe, PbTe, PbSnSe, PbSnTe, InAs, $InAs_{1-x}Sb_{1-x}$, InAsSb, III–V alloys containing Tl and Bi, and related quaternary system

materials. Among all these possible options, in the past 40 years, HgCdTe became the most important semiconductor material for infrared detectors in the mid- and long-wave infrared ranges (3–12 µm). In an effort to overcome the drawbacks of HgCdTe outlined earlier, many alternate materials have been examined, for example, HgZnTe, HgMnTe, PbSnTe, PbSnSe, InAsSb and III–V semiconductors containing Tl or Bi and low dimensional solids. The weak Hg–Te bond requires extreme care to avoid instability and non-uniformity in the bulk of the material, at surfaces, and at interfaces. Nevertheless, HgCdTe still holds the dominant position at present, mainly because it possesses a series of fine material charac- teristics. An important example is the ease of preparing infrared detectors that function at different wave bands. The lattice constant changes only 0.2% from CdTe to $Hg_{0.8}Cd_{0.2}Te$. Because of this near lattice match between different compositions stacks of layers can be built each of which corresponds to a detector that responds to a different band. Thus two-color and even multi-color pixel arrays have been built, where the different bands from a scene are in spatial register. This greatly simplifies the prob- lem of extracting information about a scene by taking advantage of this multiple band collection ability. Another benefit of the near lattice match among different compositions is the ability to grow heterojunctions in which there is little materials degradation from misfit dislocations. Curren- tly, most of the best detectors are prepared using heterojunction structures.

The lattice constant of $Hg_{1-x}(Cd_{1-y}Zn_y)_xTe$ or $Hg_{1-x}Cd_x(Te_{1-y}Se_y)$ remains almost unchanged when the composition y is adjusted by doping with small amounts of Zn or some Se, and changing x to retain a given band gap. The shorter bond length of ZnTe and CdSe forms stiffer bonds that resist bond angle distortion. This causes the energy of threading dislo- cations to increase, which tends to suppress their density. Thus the addition of suitably small amounts of Zn or Se can improve the quality of hetero- structures, with a corresponding improvement of device performance. From these examples, it is clear that the study of HgCdTe and related alloys enriches our understanding of narrow gap semiconductors and offers opportunities for innovation.

Such research is based on the fundamental physical properties of narrow gap semiconductors. It includes crystal growth, energy band structures, optical constants, lattice vibrations, excitation and transport of carriers, impurity defects, non-linear optical properties, surface–interface states, two dimensional electron gas, super-lattice and quantum wells, device physics and other new phenomena, effects and rules. These are all subjects that will be discussed in this book.

For additional information on narrow gap semiconductor physics, readers can refer to the Semimetals and Narrow-Bandgap Semiconductors

(London) by Lovett (1977), "The Properties and Applications of the HgCdTe Alloy System in Narrow Gap Semiconductors" by Dornhaus and Nimtz (1983), Springer Tracts in Modern Physics Vol. 98, p. 119, "Semiconductors and Semimetals" Vol. 18 by American scientist, collection of review thesis on HgCdTe materials and devices (Willardson and Beer 1981), "Narrow Gap Semiconductor Infrared Detectors" by Chinese scientists Dingyuan Tang and Feimin Tong (1991) ("Semiconductor research and Progress" edited by Shouwu Wang, Beijing: Science Publishing Press, pp. 1–107) and several more papers about physical and chemical properties of HgCdTe narrow gap semiconductors from "Properties of Cd-based narrow-gap compounds" compiled by Capper (1994), as well as the related data and basic formulas of HgCdTe from "Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology III/41B Semiconductors: II–VI and I–VII Compounds; Semimagnetic Compounds" republished in 1999, Germany. These references systematically discuss and review the basic physical properties of narrow gap semiconductors, theory and experimental data on these materials and on devices constructed from them.

1.2 Physics of Infrared Photo-Electronics

1.2.1 Infrared Photo-Electronics

Narrow gap semiconductor physics is one of the more important drivers of modern photo-electronics. In the twenty-first century, mankind is entering the photon technology era gradually. Applications requiring rates of hundreds of THz that cannot be accomplished with standard electronics are being done with photons. These include ultra fast computers, and communications as well as advanced imaging applications. On the one hand, people have been establishing a deeper understanding of light, its interaction with matter, and knowledge of how to control them. This background has promoted the rapid advancements of photoelectron physics, and given impetus to the development of further applications. Therefore, the field of narrow gap semiconductors is an important element in the evolution of modern photoelectron technology.

Several major problems have arisen in the research of modern photoelectron physics. As technology advances by leaps and bounds, the time between research on fundamental properties and processes, and high technology applications is becoming shorter and shorter. Moreover, high-tech application requirements have brought about more and more urgent demands on the research into fundamental laws. Even now more

demanding application requirements are the major driving force for the development of infrared photoelectron research. From the viewpoint of discipline development in the new century, infrared photoelectron physics will focus on further research on excitations, and IR photon transport and nonlinear interactions in matter. Particularly, expect further research into micro-mechanisms of conversion processes from infrared light to free carriers, from free carriers to infrared light, two infrared light sources into different frequencies, and infrared light and visible light into other visible light beams. Some of these developments will be motivated by optical computing applications.

1.2.2 Thermal Infrared Detector Materials: Uncooled Detectors

Ferroelectric thin films are a type of material that has attracted much attention in recent years. In addition to their use in the development of non-volatile memories and piezoelectric drivers, etc., they can be employed to fabricate infrared broad-bandwidth focal plane arrays (Kruse 1981) working at room temperature. This is one type of detector that falls into the class called "uncooled" detectors. The ferroelectrics function because their effective dielectric constant is temperature dependent. Because of this dependence the voltage across a charged (poled) capacitor made from such materials generates a signal in response to incident radiation as it is absorbed and heats the ferroelectric's surface. Importance is currently attached to the ferroelectric thin films PZT and BST, but it is not certain that these will ultimately prove to be the materials of choice for this application. Generally, the sol–gel method, sputtering, laser-plasma deposition, MOCVD methods and others are employed for their preparation. Research into the physics of ferroelectric thin films, their physical properties related to infrared detectors, in particular, micro mechanism of spontaneous polarization are among the hot issues under investigation in international academic and industrial circles.

A second class materials in competition for uncooled array applications are those that undergo an "insulator-to-metal" phase transition as they are heated. The type most often used at present is VO_{2-x}, where x varies between 0 and 1 (Kruse 1981). At a critical temperature these materials experience a first order phase transition in which the conductivity changes by more than four orders of magnitude. One cannot bias these materials immediately below the critical temperature to take advantage of this huge change, because devices operated in this way are unstable. However, in a range slightly below the critical temperature the material still has a sharp temperature dependence that is useful for thermal detection. VO_{2-x} also can

be vapor deposited into thin films on thin support low heat capacity structures to form arrays of detectors with practical detectivities. Their detectivities are not as good as those of cooled photon detector arrays, but they are good enough to satisfy most specifications for some applications where cooling is impractical.

1.2.3 Light Emitting Devices

As we have discussed earlier semiconductor low dimensional structures are alternative infrared photoelectric materials. Structures of III–V semiconductor quantum wells, quantum wires and quantum dots are used in preparation of infrared detectors and focal plane arrays. They were particularly touted for multi-color devices and long wavelength devices, but it is now understood that their operating modes do not allow them to hold a calibration in low light background applications. However, the relatively narrow spectral response feature of the optical transitions between sub-bands of the quantum wells is beneficial for the development of light emitting devices (LED's and Lasers). III–V semiconductor quantum wells have succeeded in emitting light in the mid-infrared wave band.

These low dimensional structures are also being developed as infrared non-linear elements for frequency multiplier and mixer applications. The preparation, control and characterization of semiconductor low dimensional structures form the basis for this direction and are an important aspect of the future development of infrared physics.

1.2.4 Processes of Infrared Physics

The core of infrared photoelectron physics research is focusing on photoelectric conversion, electro-optic conversion and photo–photo conversion processes in infrared responsive matter systems; their mechanisms and methods for controlling them. Photoelectric physics enables us to understand the conversion processes and what must be accomplished in materials processing and design to meet specific goals. These goals are often set by device specifications. Understanding the precise mechanisms also serve as the basis of device design. Thus there is a feedback loop from understanding fundamental mechanisms–fabrication strategies–device design to meet specifications–motivation for research into fundamental mechanisms, all aimed at improving performance. Of course, some research is also driven by the desire to improve man's knowledge of nature. The most important research areas are specified in the previous sections. At the moment, there

is an increasing need for various devices, such as, large-scale infrared focal plane arrays, mid-infrared wave band lasers, infrared non-linear devices and infrared mono-photon detectors, etc. These needs have imposed higher and higher requirements on research into mechanisms responsible for infrared photoelectric conversion. For example, while trends in band-to-band and trap-assisted tunneling across p–n junctions have been known for years, no quantitatively reliable theory exists. This knowledge is needed to improve the performance of LWIR focal plane arrays.

Efforts are still underway to discover more quantitative relationships between the photoelectric conversion process and energy band structures, impurity defects and lattice vibrations in order to obtain clearer physical patterns and models. In the past, a relatively deep study of the photo-electric process in three-dimensional systems had been made. Now, it is necessary to study these effects in 2D electron gases at surfaces and interfaces, at impurity defects, and in clusters of concentration fluctuation related quantum dots. New approaches should be explored to advance our knowledge base in each of these areas.

The mechanisms and materials involved in photoelectric emission devices comprise a different set of research areas. Stimulated emission light sources and free electron lasers mostly made from III–V compound alloy based micro-structures, are electro-optic converters covering wide spectral ranges including the entire infrared wave band. These materials and device structures are major subjects of worldwide investigation. The physics of the electro-optic conversion process in these systems is also another hot issue for study. Other major research drivers are the need for high-speed optical switches, electro-optic modulators, mid-infrared lasers, and THz sources. People have worked diligently to discover the physical process responsible limits on high-speed electro-optic modulation and the process of photo-excited emission in mid-infrared. Significant progress has been achieved in the research on electro-optic modulation of GaAlAs based super-lattice structures, on quantum dots lasing of InGaAs, and cascade laser emission of InAsSb based complex super-lattice systems.

Opto-optic mixers require materials transparent over the incident and the mixed frequency bands and having non-linear dielectric constants. Research efforts focus on the mechanisms responsible for the mixing phenomena in new materials, particularly exploration the non-linear optical response of solid low dimensional structures. These are currently active research issues in the infrared field.

Research has always been an essential element in making progress with the interaction between photons and the electrical response of materials. Most future developments will depend on complete accurate physical models based on fundamental precepts. Exploration of new photoelectric

testing and measuring methods, are likely paths to unearthing new phenomena, and new device opportunities. Active research in these areas is continuing in various parts of the world without any sign of decline.

1.2.5 Infrared Materials Research, Device, and Applications Status

Infrared photon device physics is the basis of most device applications. Infrared photon devices cover a collection of infrared applications, including large-scale infrared focal plane arrays for cameras, infrared single photon detectors for high speed communications and astronomy, mid-infrared lasers for scientific instruments, etc.

Large-scale infrared focal plane arrays at present are the most advanced third generation infrared scene sensors. They collect information by focusing a scene on the detector array. The IR (infrared) photons striking an element of the array (a pixel) excite carriers in proportion to the intensity of that spot in the scene. In the most sophisticated arrays intensity distributions at several parts of the IR spectrum are separately detected at each pixel. Periodically, at a specified frame rate, the signals generated by the elements of the array are read out by a read-out-integrating-circuit (ROIC). This information is then displayed on a monitor, and processed to extract information about the scene. Arrays that function in this fashion are called "staring arrays"; they have almost completely replaced the older "scanning" systems. The simplest version of a scanning system employs a moveable mirror to scan different regions of a scene sequentially onto a single detector.

Staring arrays have been constructed from narrow gap semiconductors, from quantum well devices operating at low temperature; and from ferroelectrics and insulator-to-metal thin film devices operating at room temperature. The use of staring focal plane arrays has not only greatly simplified the structure of imaging systems, and improved their reliability, but has also increased their detecting performance remarkably. The images and their spectral content obtained from these systems have been used for target tracking, recognition, and even for quantitative analysis of the nature of the materials in the scene. The images have yielded valuable information both on macro objects, such as the health of forests, ground waters, and meteorology data; and on micro objects, such as biological cells.

Although considerable research progress has been made on the fundamental behavior of the materials used in photon detectors, and theories exist that properly predict observed trends and in some cases even

quantitative properties, there still are quantitative physical problems that are unresolved. Modern theoretical techniques are gradually eliminating the remaining uncertainties (Chen and Sher 1995). For example, the advent of density functional theory (DFT) has allowed us to calculate, with no adjustable parameters and with remarkable precision, ground state crystal structures, including their bond lengths and elastic constants, as well as the band structures of all the group IV elements and the III–V, and II–VI compound semiconductors. These DFT methods are computationally intensive, but a theory called the hybrid pseudo-potential tight-binding (HPT) theory, while it depends on a few adjustable pseudo-potential form factors for each material, yields equally accurate band structures and wave functions. The form factors can be extracted from the DFT predictions, so it can be argued that HPT results are also parameter free. The HPT theory is much more manageable, and can be coupled with the coherent potential approximation (CPA) method to calculate, in excellent agreement with experiment, the band structures and wave functions of the alloys of all these semiconductors. The quality of the wave functions can be judged from the excellent agreement between the predictions of the temperature and concentration variations of the band gaps for several semiconductors and alloys including HgCdTe (Krishnamurthy et al. 1995). For this result to be reached, the matrix elements of the electron–phonon interactions had to be accurate. Numerous other physical processes can now be predicted in agreement with experiment, e.g. absorption coefficients, carrier transport properties, densities of native point defects as functions of temperature and partial pressures covering the whole stability region for all alloy concentrations, etc. However, there do remain unresolved problems that impact device performance, and as growth processes and device designs improve to overcome old barriers to performance, new challenges constantly arise. Examples include improved control of impurities and extended defects, surface passivation, tunneling through hetero-junctions, and the origin of 1/f noise. An example of a breakthrough in the new era would be LWIR photon based focal plane arrays operating at room temperature. Accomplishing this goal would involve somehow tricking nature to overcome the adverse effects of thermally excited carriers.

A fast infrared single photon detector is another important quantum device with major applications in the giga- to tera-Hertz information transmission field. There are special needs for infrared single photon detectors operating in the 1.3 and 1.55 μm wave bands. These bands are where current optical fiber materials have low absorption coefficients. Development of InGaAs based avalanche photodiodes is an important topic in the development of infrared single photon detectors; and significant progress has been achieved. Other competitors for this

application are HgCdTe and HgMnTe with their concentrations chosen so their spin–orbit split-off band and forbidden band gap energies match. This is beneficial to a "resonant ionization by collision" phenomenon in the wave band range of 1.3–1.8 µm, which can yield avalanche photodiodes with high gain and low noise. With a proper composition ratio, a quarternary system HgCdMnTe can be used to prepare an avalanche photodiode with its maximum response at 1.55 µm. Therefore, another important frontier subject at present is research into the absorption and recombination process among conduction bands, valence bands and spin–orbit split bands as well as the theory of the avalanche ionization process. This will help to develop optimum sensitivity HgCdTe, HgMnTe, InGaAs avalanche photodiodes, and to explore other candidate single photon detector mechanisms.

Mid wave band infrared lasers are another important research subject. This activity was initiated at the end of the last century. Now people have started to use III–V semiconductor quantum well structures to prepare mid-infrared cascade lasers, and this work will go forward in the new century. Research on quantum dot lasers, quantum dot infrared detectors and attempts to devise infrared focal plane arrays without attached read-out circuits will be carried out vigorously in the new era.

References

Arias JM, Shin SH, Pasko JG, DeWames RE, Gertner ER (1989) Long and middle wave length infrared photodiodes fabricated with $Hg_{1-x}Cd_xTe$ grown by molecular beam epitaxy. J Appl Phys 65:1747–1753

Arias JM, Pasko JG, Zandian M, Shin SH, Williams GM, Bubulac LO, DeWames RE, Tennant WE (1993) MBE HgCdTe heterostructure p-on-n planar infrared photodiodes. J Electron Mater 22:1049–1053

Brill G, Velicus, Boieriu P, Brill G, Velicu S, Boieriu P, Chen Y, Dhar NK, Lee TS, Selamet Y, Sivananthan S (2001) MBE growth and device processing of MWIR HgCdTe on large area Si substrates. J Electron Mater 30:717–722

Capper P (1994) In: Capper P (ed) Properties of Cd-based narrow-gap Compounds. London, INSPEC/IEE

Chapman CW (1979) The state of the art in thermal imaging: Common modules. In: Electro-Optics/Laser 79'Conference and Exposition, Anaheim, California, USA, Oct. 23–25, 1979. Industrial and Scientific Conference Management, Chicago, pp. 49–57

Chen AB, Sher A (1995) Semiconductor Alloys. Plenum Press, New York

Choi HK, Eglash SJ (1992) High-power multiple-quantum-well GaInAsSb/AlGaAsSb diode lasers emitting at 2.1 µm with low threshold current density. Appl Phys Lett 61:1154–1156

Choi HK, Turner GW (2000) Antimonide-based mid-infrared lasers. In: Helm M (ed) Long wavelength infrared emitters based on quantum wells and super-lattices. Gordon and Breach Science Publishers, Singapore, Chapter 7

Dingyuan Tang (1974) Properties of ternary system HgCdTe semiconductors. Infrared Physics and Technique, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 16:345

Dingyuan Tang (1976) HgCdTe material for infrared detectors. Infrared Physics and Technique, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 4–5:53

Dingyuan Tang, Feiming Tong (1991) Narrow gap semiconductor infrared detectors. In: Shouwu Wang (ed) Development of Semiconductor Devices and Progress. Science Publishing Press, Beijing, pp. 1–107

Dornhaus R, Nimtz G (1983) The properties and applications of the HgCdTe alloy system. In: Narrow Gap Semiconductors, Spring Tracts in Modern Physics, Vol. 98. Springer, p. 119

Elliot CT (1981) New Detector for Thermal Imaging Systems. Electron Lett 17: 312–314

Faurie JP, Million A, Piaguet J (1982) CdTe–HgTe multilayers grown by molecular beam epitaxy. Appl Phys Lett 41:713–715

Harman TC (1980) Liquidus isotherms, solidus lines and LPE growth in the Tellurium-Rich corner of the HgCdTe System. J Electron Mater 9:945–961

Irvine SJC, Mulin JB (1981) The growth by MOVPE and characterization of $Cd_xHg_{1-x}Te$. Thin Solid Films 90:107–102

Kane EO (1957) Band structure of indium antimonide. J Phys Chem Solids 1:249–261

Kane EO (1966) Semiconductors and Semimetals Vol. 1. Academic press, London, p. 75

Kane EO (1981) Narrow Gap Semiconductors: Physics and Applications. Springer-Verlag, Berlin

Krishnamurthy S, Chen AB, Sher A, Van Schilfgaarde M (1995) Temperature dependence of band gaps in HgCdTe and other semiconductors. J Electron Mater 24:1121–1125

Kruse PW (1981) The emergence of $Hg_{1-x}Cd_xTe$ as a modern infrared sensitive material. In: Willardson RK and Beer AC (eds) Semiconductors and Semimetals, Vol. 18. Academic press, London, pp. 1–20

Lawson WD, Nielson S, Putley EH, Young AS (1959) Preparation and properties of HgTe and mixed crystals of HgTe–CdTe. J Phys Chem Solids 19:325–329

Levine BF (1993) Quantum-well infrared photodetectors. J Appl Phys 74:R1–R81

Levine BF, Choi KK, Bethea CG, Walker J, Malik RJ (1987) New 10 μm infrared detector using intersubband absorption in resonant tunneling GaAlAs superlattices. Appl Phys Lett 50:1092–1094

Long D, Schmit JL (1973) Infrared Detectors. Academic Press, New York

Lovett DR (1977) Semimetals and Narrow-bandgap Semiconductors. In: Goldsmid HJ, Ballentyne DWG (eds) Applied Physics Series. Pion Limited, London

Micklethwaite WFH (1981) The crystal growth of Cadmium Mercury telluride. In: Willardson RK, Beer AC (eds) Semiconductors and Semimetals, Vol. 18. Academic Press, London, pp. 70–84

Schmit JL, Bowers JE (1979) LEP growth of $Hg_{0.60}Cd_{0.40}Te$ from Te-rich solution, Appl Phys Lett 35:457–458

Stelzer EL, Schmit JL, Tufte ON (1969) Mercury Cadmium Telluride as an infrared detector material. IEEE Trans. Electron Devices 16:880–884

Varesi JB, Bornfreund RE, Childs AC, Radford WA, Maranowski KD, Peterson JM, Johnson SM, Giegerich LM, de Lyon TJ, Jensen JE (2001) Fabrication of high-performance large-format MWIR focal plane arrays from MBE-grown HgCdTe on 4 inch silicon substrates. J Electron Mater 30:566–573

Willardson RK, Beer AC (1981) Mercury cadmium telluride. In: Willardson RK, New York

2 Crystals

2.1 Theory of Crystal Growth

2.1.1 Introduction

The $Hg_{1-x}Cd_xTe$ Narrow gap semiconductors are nearly random substitutional alloys of the II–VI binary compounds CdTe and HgTe. The fraction (composition) of CdTe is x and of HgTe is 1-x. The ground states of the HgTe and CdTe compounds as well as the $Hg_{1-x}Cd_xTe$ alloys for all compositions x, have zincblende cubic structures (Daruhaus and Vimts 1983). In this crystal structure there are two interpenetrating face centered cubic sub-lattices, one occupied by the Te anions, and the other shared by the Cd and Hg cations The two interpenetrating face-centered cubic lattices are offset with respect to one another by the displacement $\left(\frac{1}{4}a_0, \frac{1}{4}a_0, \frac{1}{4}a_0\right)$, where a_o is the cube edge length, i.e., the lattice constant. The lattice constant of the HgTe crystal is 6.46 Å, and that of CdTe is 6.48 Å. In Fig. 2.1, cations (Cd or Hg) are listed as type A while Te anions are type B.
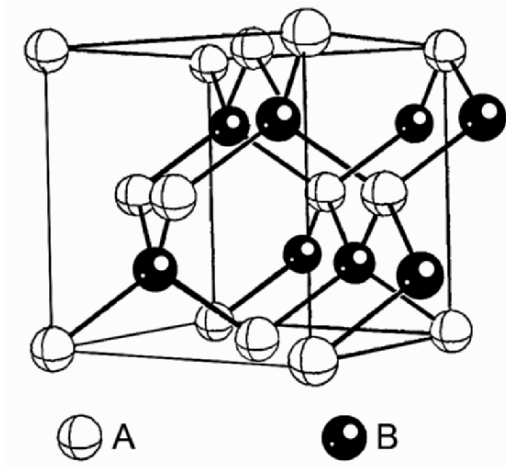

Fig. 2.1. Zincblende crystal structure