Ghenadii Korotcenkov *Editor*

Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors

Volume 1, Materials and Technology

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Editor
Ghenadii Korotcenkov
Department of Physics and Engineering
Moldova State University
Chisinau, Moldova

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Preface

Binary and ternary semiconductors of II-VI group (ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgTe, HgS, HgSe, HgCdTe, CdZnTe, CdSSe, and HgZnTe) are very popular among researchers because of their remarkable physical and chemical properties, which, as a group, are unique. II-VI compounds possess a very wide spectrum of electronic and optical properties. Most materials of group II-VI are semiconductors with a direct band gap and high optical absorption and emission coefficients. In addition, binary II-VI compounds are easily miscible, providing a continuous range of properties. As results, the II-VI semiconductors possess band gap, varying over a wide range. Therefore, II-VI compounds can serve as efficient light emitters, such as light diodes and lasers, solar cells, and radiation detectors operating in the range from IR to UV and X-ray. II-VI compound-based devices can also cover terahertz range. Besides common photovoltaic applications, II-VI semiconductors are also potential candidates for a variety of electronic, electro-optical, sensing, and piezoelectric devices. In particular, nanoparticles of II-VI semiconductors, such as quantum dots, one-dimensional structures, and core-shells structures, can be used for development of gas sensors, electrochemical sensors, and biosensors. These semiconductors, when downsized to nanometer, have become the focus of attention because of their tunable band structure, high extinction coefficient, possible multiple exciton generation, and unique electronic and transport properties. It is important that II-VI semiconductors can be easily prepared in high quality epitaxial, polycrystalline, and nanocrystalline films. The concentration of charge carriers can also vary in II-VI semiconductors in wide range due to doping. Thus, the use of II-VI films represents an economical approach to the synthesis of semiconductors for various applications. It should be noted that the range of technical applications for II-VI compounds goes beyond the better-known semiconductors such as Si, Ge, and some of III-V compounds.

Formally, metal oxides such as CdO and ZnO also belong to II-VI compounds. However, we will not cover them in this book. In recent years, these compounds have been allocated to a separate group, “metal oxides,” and many books have been devoted to their discussion, in contrast to other II-VI compounds. In particular, those who are interested in exactly these compounds, we can recommend the Metal Oxides series which is published by Elsevier.

The aim of this three-volume book is to provide an updated account of the state of the art of multifunctional II-VI semiconductors, from fundamental sciences and material sciences to their applications as various sensors and radiation detectors, and, based on this knowledge, formulate new goals for further research. This book provides interdisciplinary discussion of a wide range of topics, such as synthesis of II-VI compounds, their deposition, processing, characterization, device fabrication, and testing. Topics of the recent remarkable progresses in application of nanoparticles, nanocomposites, and nanostructures consisting of II-VI semiconductors in various devices are also covered. Both experimental and theoretical approaches were used for this analysis.

Currently, there exist books on II-VI semiconductors. However, some of them were published too long ago and cannot reflect the current state of research in this area. Other published books focus on a limited number of topics, from which topics related to various sensor applications such as gas sensors, humidity sensors, and biosensors are almost completely excluded. When considering photodetectors, the focus is also only on the analysis of IR photodetectors. Although sensors operating in the visible, ultraviolet, terahertz, and X-ray ranges also hold great promise for applications. With these books, we will try to close this gap.

Our three-volume book *Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors* is the first to cover both chemical sensors and biosensors and all types of photodetectors and radiation detectors based on II-VI semiconductors. It contains a comprehensive and detailed analysis of all aspects of the application of II-VI semiconductors in these devices. This makes these books very useful and comfortable to use. Combining this information in three volumes, united by common topics, should help readers in finding the necessary information on required subject.

Chapters in *Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors. Vol. 1: Materials and Technologies* describe the physical, chemical, and electronic properties of II-VI compounds, which give rise to an increased interest in these semiconductors. Technologies that are used in the development of various devices based on II-VI connections are also discussed in detail in this volume.

Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors. Vol. 2: Photodetectors focuses on the consideration of all types of optical detectors, including IR detectors, visible detectors, and UV detectors. This consideration includes both the fundamentals of the operation of detectors and the peculiarities of their manufacture and use. An analysis of new trends in development of II-VI semiconductors-based photodetectors is also given.

Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors. Vol. 3: Sensors, Biosensors and Radiation Detector describes the use of II-VI compounds in other fields such as radiation detectors, gas sensors, humidity sensors, optical sensors, and biosensors. The chapters in this volume provide a comprehensive overview of the manufacture, parameters, and applications of these devices.

We believe that these books will enable the reader to understand the present status of II-VI semiconductors and their role in the development of new generation of photodetectors, sensors, and radiation detectors. I am very pleased that many well-known experts with extensive experience in the development and research of II-VI semiconductor sensors and radiation detectors were involved in the preparation of the chapters of these books.

The target audience for this series of books are scientists and researchers working or planning to work in the field of materials related to II-VI semiconductors, i.e., scientists and researchers whose activities are related to electronics, optoelectronics, chemical and bio sensors, electrical engineering, and biomedical applications. I believe this three-volume book may also be of interest to practicing engineers and project managers in industries and national laboratories who would like to develop II-VI semiconductor-based radiation sensors and detectors but do not know how to do it, and how to select the optimal II-VI semiconductor for specific applications. With numerous references to an extensive resource of recently published literature on the subject, these books can serve as an important and insightful source of valuable information, providing scientists and engineers with new ideas for understanding and improving existing II-VI semiconductor devices.

I believe that these books will be very useful for university students, doctoral students, and professors. The structure of these books offers the basis for courses in materials science, chemical engineering, electronics, optoelectronics, environmental control, chemical sensors, photodetectors, radiation detectors, biomedical applications, and many others. Graduate students may also find the book very useful in their research and understanding of the synthesis of II-VI semiconductors, study, and application of this multifunctional material in various devices. We are confident that all of them will find the information useful for their activities.

Finally, I thank all the authors who contributed to these books. I am grateful that they agreed to participate in this project and for their efforts to prepare these chapters. This project would not have been possible without their participation. I am also very grateful to Springer for the opportunity to publish this book with their help. I would like also to inform that my activity related to editing this book was funded by the State Program of the Republic of Moldova project 20.80009.5007.02.

I am also grateful to my family and wife, who always support me in all my endeavors.

Chisinau, Moldova Ghenadii Korotcenkov

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About the Editor

Ghenadii Korotcenkov received his PhD in physics and technology of semiconductor materials and devices in 1976 and his Doctor of Science degree (doctor habilitate) in physics of semiconductors and dielectrics in 1990. He has more than 50-year experience as a teacher and scientific researcher. For a long time, he was a leader of gas sensor group and manager of various national and international scientific and engineering projects carried out in the Laboratory of Micro- and Optoelectronics, Technical University of Moldova, Chisinau, Moldova. International foundations and programs such as the CRDF, the MRDA, the ICTP, the INTAS, the INCO-COPERNICUS, the COST, and NATO have supported his research. From 2007 to 2008, he carried out his research as an invited scientist at Korea Institute of Energy Research (Daejeon). Then, from 2008 to 2018, Dr. G. Korotcenkov was a research professor in the School of Materials Science and Engineering at Gwangju Institute of Science and Technology (GIST) in Korea. Currently, G. Korotcenkov is a chief scientific researcher at Moldova State University, Chisinau, Moldova.

Scientists from the former Soviet Union know the results of G. Korotcenkov's research in the study of Schottky barriers, MOS structures, native oxides, and photoreceivers based on III–Vs compounds such as InP, GaP, AlGaAs, and InGaAs. His current research interests since 1995 include material sciences, focusing on metal oxide film deposition and characterization (In_2O_3, SnO_2, ZnO, TiO_2), surface science, thermoelectric conversion, and design of physical and chemical sensors, including thin film gas sensors.

G. Korotcenkov is the author or editor of 45 books and special issues, including the 11-volume "Chemical Sensors" series published by Momentum Press; 2-volume "Handbook of Gas Sensor Materials" published by Springer; 15-volume "Chemical Sensors" series published by Harbin Institute of Technology Press, China; 3-volume "Porous Silicon: From Formation to Application" issue published by CRC Press; 3-volume "Handbook of Humidity Measurements" published by CRC Press; 3-volume "Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors" published by Springer; and 6 proceedings of the international conferences published by Trans Tech Publ., Elsevier, and EDP Sciences. In addition, currently he is a series editor of "Metal Oxides" book series published by Elsevier. Since 2017, more than 35 volumes have been published within this series.

G. Korotcenkov is the author and coauthor of more than 650 scientific publications, including 9 review papers, 38 book chapters, and more than 200 peer-reviewed articles published in scientific journals (h-factor = 43 (Web of Science), h = 45 (Scopus) and h = 61 (Google scholar citation), 2022). He is the holder of 17 patents. He presented more than 250 reports at the National and International conferences, including 17 invited talks. G. Korotcenkov, as a cochairman or member of program, scientific, and steering committees, has participated in the organization of more than 40 international scientific conferences. Dr. G. Korotcenkov is a member of editorial boards in five scientific international journals. His name and activities have been listed by many biographical publications including Who's Who. G. Korotcenkov have also been listed as one of the "World's Ranking Top 2% Scientists" in Applied Physics/Analytical Chemistry in the Physics and Astronomy Cluster. His research activities have been honored by the National Prize of the Republic of Moldova (2022), the Honorary Diploma of the Government of the Republic of Moldova (2020), an Award of the Academy of Sciences of Moldova (2019), an Award of the Supreme Council of Science and Advanced Technology of the Republic of Moldova (2003), the Prize of the Presidents of the Ukrainian, Belarus, and Moldovan

Academies of Sciences (2004), Senior Research Excellence Award of Technical University of Moldova (2001; 2003; 2005), the National Youth Prize of the Republic of Moldova in the field of science and technology (1980), among others. Some of his research results and published books have won awards at international exhibitions. G. Korotcenkov also received a fellowship from the International Research Exchange Board (IREX, United States, 1998), Brain Korea 21 Program (2008–2012), and BrainPool Program (Korea, 2007–2008 and 2015–2017).

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Part I
II-VI Semiconductors Properties

Chapter 1
Introduction in II-VI Semiconductors

Osvaldo de Melo

1.1 Introduction

II-VI semiconductors are composed by elements of the groups IIB (12 in the modern classification, or Zn family group) and VIA (16 in the modern classification or chalcogen group) of the periodic table (see the relevant section in Table 1.1). Along this book, mainly compounds and alloys formed of Zn, Cd, and Hg, from the group IIB, and the chalcogen elements S, Se, and Te from the group VIA will be considered. Oxygen, an important member of the VIA group which forms semiconducting compounds with IIB elements, is often classified in the more specific group of oxides. Cn (copernicium) and Lv (livermorium) are recently discovered member of the IIB and VIA group, respectively, but they are artificial and unstable without any practical interest in materials science. Polonium, belonging to the VIA group, is a very rare element. On the other hand, Be and Mg from the group IIA can form semiconducting compounds when mixing with chalcogen elements; they are frequently used in alloys for tuning the lattice parameter or band gap in heterostructures.

This introductory chapter is divided into four parts corresponding to aspects that, in the opinion of the author, can motivate the reader to face the book or help him to grasp the different topics in the next chapters. First, a brief journey through the history of II-VI semiconducting compounds and related materials will allow the reader to appreciate the origins and development of these important materials. In the following section, an account will be presented of the main basic properties that distinguish II-VI compounds and make them useful for fabricating different kinds of devices for a wide variety of applications. This section summarizes important topics

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O. de Melo (✉)
Physics Faculty, University of Havana, La Habana, Cuba
e-mail: omelo@fisica.uh.cu

G. Korotcenkov (ed.), *Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors*, https://doi.org/10.1007/978-3-031-19531-0_1

Table 1.1 Section of the periodic table where II-VI semiconducting compounds are located. Relevant elements from IIB and VIA groups are highlighted

Row ↓	Group →	11	**12 (IIB)**	13	14	15	**16 (VIA)**	17
				B	C	N	O	F
3				Al	Si	P	**S**	Cl
4		Cu	**Zn**	Ga	Ge	As	**Se**	Br
5		Ag	**Cd**	In	Sn	Sb	**Te**	I
6		Au	**Hg**	Tl	Pb	Bi	Po	
7			Cn				Lv	

such as the fundamentals of fabrication of alloys and heterostructures, conductivity type and dopability control, and nanostructures synthesis and properties. Finally, in the last section, the main areas in which applications have been developed or in which there is potential for applications of II-VI compounds are briefly resumed.

1.2 The History of II-VI Semiconductors: A Brief Journey

Chalcogen elements were important components of early semiconductor materials. More than 2000 years ago, in the Greco-Roman period, a hair dyeing formula used a cream composed by PbO and $Ca(OH)_2$ for blackening the hair. Today, it is known that lead reacted with the sulfur in the amino acids of hair to form small crystals of PbS, similar to the PbS quantum dots that scientists fabricate today routinely [1]. Much later, silver sulfide was the first discovered material with semiconducting behavior (electrical conductivity increase with temperature) as early as in 1833 by Michael Faraday who described his experience in an expressive way:

> There is no other body with which I am acquainted, that, like sulphuret of silver, can compare with metals in conducting power for electricity of low tension when hot, but which, unlike them, during cooling, loses in power, whilst they, on the contrary, gain. Probably, however, many others may, when sought for, be found. [2]

What today is known as photovoltaic effect was first observed in selenium crystals in 1877 [3], while electric current rectification was detected in selenides in the same decade. PbS (with the mineral name galena) reappears in the history as the material forming the first signal detector. It was developed by Karl Ferdinand Braun [4] who shared the Nobel Prize in physics in 1909 with Guglielmo Marconi for their “contributions to the development of wireless telegraphy.”

II-VI compounds are a well-established family that celebrated their first congress in Rhode Island as early as in 1967 with the name of II-VI Semiconducting Compounds International Conference. After 15 years, the conference series was recommenced as the International Conference of II-VI compounds which has held in Durham (1983), Aussois (1985), Monterrey (USA) (1987), Berlin (1989), Tamano (1991), Rhode Island (1993), Edinburgh (1995), Grenoble (1997), Kyoto (1999), Bremen (2001), Niagara Falls (2003), Warsaw (2005), Jeju (2007), St. Petersburg (2009), and Riviera Maya (2011). From this year on, the topics of the conference were extended to include related compounds as chalcopyrites, different kinds of oxides, and 2D materials. The name of the series was modified to “International Conference of II-VI compounds and Related Materials” with the next meetings in Nagahama (2013), Paris (2015), San Juan (2017, the in-person event was affected by the occurrence of Hurricane Maria), Zhengzhou (2019), and Bath (2022).

1.3 Material Properties

1.3.1 General Trends: Chemistry, Structure and Band Gaps

As expected, according to their position in the periodic table, II-VI compounds have more ionic bonds than III-V compounds and, obviously, than elemental semiconductor of the group IV which are completely covalent materials. For example, the fractional ionic character for compounds in the fourth row CuBr (I-VII), ZnSe (II-VI), GaAs (III-V), and Ge (IV) are 0.735, 0.63, 0.31, and 0, respectively [5]. Due to the large iconicity, II-VI compounds tend to present larger band gaps than the other semiconductor groups, so, CuBr, ZnSe, GaAs, and Ge present band gaps of 2.94, 2.7, 1.4, and 0.66 eV, respectively.

Differently from III-V compounds, II-VI materials tend to evaporate congruently due to the higher vapor pressure of the group II elements compared with those of group III elements. This is the reason why simple and low-cost vapor phase techniques as thermal evaporation or close space vapor transport are widely used for preparing polycrystalline II-VI materials. In the phase diagrams, only the stoichiometric II-VI compound solid appears, while the vapor phase is composed by atomic monomers of the group II element and dimers or polymers of the group VI element.

Most frequent crystal structures in II-VI semiconductors are wurtzite, with hexagonal symmetry, or sphalerite (also called zinc blend in reference to the II-VI ZnS mineral) with cubic symmetry, which are displayed in the left panel of Fig. 1.1. In both structures, there is tetrahedral coordination, and the two different lattice sites are occupied by the IIB and VIA elements, respectively. In some compounds such as CdS and CdSe, for example, the free energy difference between both phases is quite small, and they can be found in both structures quite stably; they can even coexist in the same sample.

Interesting features of II-VI compound can be appreciated in the right panel of Fig. 1.1 in which the room temperature band gap is plotted as a function of the lattice

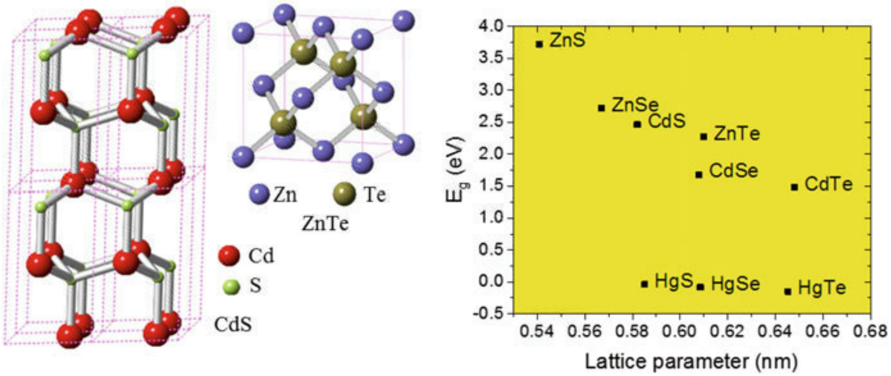

Fig. 1.1 Hexagonal wurtzite and cubic sphalerite structures common in II-VI compounds illustrated with CdS (wurtzite) and ZnTe (sphalerite) compounds, respectively (left). Room temperature energy band gap and lattice parameters for the II-VI compounds in the cubic structure (right)

parameter for all the II-VI compounds [6] in the cubic structure.[1] The band gap is direct for all the compounds having a band gap and ranges from nearly zero for Hg compounds to 3.7 eV for ZnS. This allows the fabrication of photonics detectors and other devices in a large range of wavelengths: from the far infrared up to the ultraviolet and even in the X-ray and gamma ray spectral regions.

1.3.2 II-VI Semiconductor Alloys

To tune the band gap or the lattice constant (or both), alloys can be synthesized from the different compounds. In the case where the two binary extrema of these alloys are in the same crystallographic modification, solubility is expected to exist in all the composition range. Then, they can be represented as $A_xB_{1-x}C$ or AC_xD_{1-x} where A and B stand for IIB group elements while C, D for group VIA elements (alternatively, the notation $(AC)_x(BC_{1-x})$ or $(AC_x)(AD_{1-x})$ is frequently used). Although these alloys are formed by three elements, they are not considered as true ternary alloys since the composition is specified by a single parameter: one of the elements occupies one of the two sites of the crystal lattice, while the other site is shared by the other two elements. Important examples of these alloys are the semiconductors $Hg_{1-x}Cd_xTe$ and $Cd_{1-x}Zn_xTe$. In these kinds of alloys, the lattice parameter a varies quite linearly with the composition x; so, for an alloy $A_xB_{1-x}C$, the empirical Vegard Law holds and $a = xa_{AC} + (1-x)a_{BC}$ (a_{AC} and a_{BC} are the lattice parameters of the binary extrema compounds). Due to the similarity of the ionic radii of Hg and Cd, it is

---

[1] Slight increase of the band gap is observed for the wurzite structure with respect to the cubic structure. For example, wurzite CdS (a = 0.416 nm; b = 0.6756 nm) presents a band gap of 2.501 eV, slightly higher that 2.46 eV for the cubic structure.

interesting to note that for $Hg_{1-x}Cd_xTe$ (or any other pseudobinary alloy containing Hg and Cd), the lattice parameter of the alloy is quite independent of the composition.[2] This fortunate issue allows using CdTe substrates for growing epitaxial films of $Hg_{1-x}Cd_xTe$ at every composition. When the mixed compounds have different crystallographic phases, solubility occurs only near the extreme compositions 0 and 1. This occurs, for example, in the CdS_xTe_{1-x} alloy, which is usually formed in the CdTe/CdS interface of the CdTe-CdS solar cells.

The band gap of pseudobinary alloys also varies with composition but not linearly; in general, a bowing parameter has to be considered and the equation relating the band gaps of the compounds $E_{g\ AC}$ and $E_{g\ BC}$ with the band gap of the alloy E_g is usually written as $E_g = xE_{g\ AC} + (1 - x)E_{g\ BC} + Bx(1 - x)$ where B is the bowing parameter. The band gap and lattice parameter of the compounds or alloys can be further modified by strain or by quantum confinement in samples in which at least one dimension is below the Bohr exciton ratio. In this case, it is common to speak of quantum wells, wires, or dots with 1D, 2D, or 3D confinement, respectively. More complex multinary alloys involving only II-VI compounds, including elements for other groups of the periodic table, or even inorganic compounds, have been also obtained and studied [7].

1.3.3 Band Alignment and Heterostructures

An important parameter for heterostructure-based devices is the band alignment that allows favoring or blocking the injection of the desired carriers (electron or holes) through the interfaces. This ability is in the heart of the operation of any electronic or optoelectronic device. Barrier materials in quantum-confined devices as quantum wells or wires, or core/shell nanostructures must have larger band gap than the confined material but also an adequate conduction and valence band alignment if both types of carriers must be confined: the conduction/valence band of the barrier lying over/below the conduction/valence band of the well. This is known as type I band alignment.

The band location for II-VI compounds (with respect to the vacuum level, taken as zero reference energy for all compounds) is illustrated in Fig. 1.2a in which electron affinity (χ_e) and band gap of the different compounds were taken from ref. [8], except for Hg chalcogenides in which case data was obtained from valence band maximum calculations [9, 10].

Some examples of structures that take advantage of the band alignment are also presented in Fig. 1.2. ZnSe/CdSe/ZnSe heterostructure (Fig. 1.2b for two different wells thickness) can form a type I quantum structure in which ZnSe forms a barrier for both electrons and holes. For very thin CdSe layers, this type of structure is

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[2] In this sense II-VI alloy $Hg_{1-x}Cd_xTe$ alloys is similar to its III-V counterpart $Ga_{1-x}Al_xAs$ in which the lattice parameter is practically unchanged with composition.

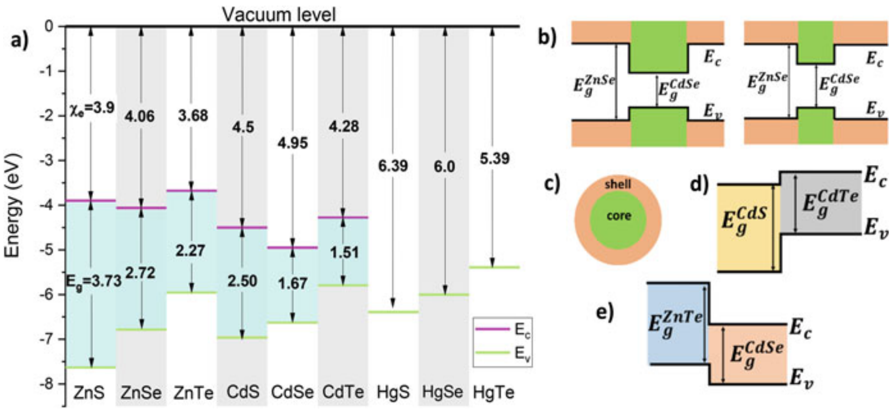

Fig. 1.2 (**a**) Band gap alignment for II-VI compounds. (**b**) Band alignment in the ZnSe/CdSe/ZnSe quantum structure. For very small well size, the band gap increases because of the quantum confinement effect. (**c**) A core-shell structure with similar shell (barrier) well (core) band alignment. (**d** and **e**) Band alignments for the CdS/CdTe heterostructure solar cell and a ZnTe/CdSe photodetector

highly luminescent, and the characteristic emission can be varied in a wide wavelength range by changing the thickness of the CdSe layer [11]. As it will be described in the next section, the same type I configuration occurs in core/shell nanostructures with ZnSe or ZnS shells (barriers) as shown in Fig. 1.2c. It can be noted that ZnS, due to its large band gap and the energy location of its bands extrema, can be used as a barrier for practically all other II-VI compounds and even for semiconductors of other groups. ZnS has other two important advantages: it is not toxic, and both Zn and S are abundant materials in the earth crust. The band alignment in the CdS/CdTe heterostructure solar cell is shown in Fig. 1.2d. In this structure, the alignment favors the injection of holes/electrons in the CdS/CdTe layer as needed for the photocurrent in a solar cell. Figure 1.2e shows a ZnTe/CdSe core/shell nanowire structure that use the piezo-phototronic effect [12].

1.3.4 Conductivity Type and Doping

The main problems faced in the early development of II-VI semiconducting compounds were related with the control of the conductivity and the doping ability. They arise because of self-compensation by defects, low solubility limits, or reactivity of dopants. In fact, in II-VI compounds, some intrinsic defects can lead to the formation of relatively shallow levels in the band gap which play an important role in the conductivity value, in the conductivity type, and in the compensation mechanisms. Some of the problems related to doping have been partially solved by using nonequilibrium growth techniques such as molecular beam epitaxy (MBE) or metal organic vapor phase epitaxy (MOVPE) that remove some of the equilibrium thermodynamics restrictions using lower temperatures and obtaining films with low defects density and the desired impurification. The use of plasma sources in MBE has allowed to dope with atomic elements which are not present in the equilibrium vapor species; this has been used to obtain p-type ZnSe by doping it with atomic nitrogen, for example.

Thus, for non-intentionally doped materials, as a trend, anion (element of the group II) vacancies or cation (element of the group VI) interstitials lead to n-type conductivity, while cation vacancies or anion interstitial lead to p-type conductivity. So, to a large extent, conductivity has been controlled by adequate annealing processes that modify the stoichiometry of the compound. For example, as-grown $Hg_{1-x}Cd_xTe$ is frequently encountered with p-type conductivity because of the presence of vacancies of the volatile element mercury [13]. These vacancies can be eliminated by post-growth annealing in Hg vapors of by using an adequate Hg overpressure during the growth of the films. In the case of CdS, sulfur annealing contribute to a decrease of the red luminescent band ascribed to sulfur vacancies defects and to increase the conductivity in two orders of magnitude [14]. In general, it has been observed that undoped tellurides tend to be p type and undoped sulfides tend to be n types. In the case of selenides, undoped ZnSe tends to be n-type, and CdSe has been found with both p-type and n-type conductivity.

More control of the carrier concentration and the conductivity type can be obtained using extrinsic doping. So, group I/group V elements when substituting the cation/anion lead to p-type conductivity, while group III/group VII substituting the anion/cation leads to n-type conductivity. The doping of II-VI compounds and alloys is a very exciting topic presently. The goal is to find the adequate dopants and methods that allow to obtain controlled and relatively high values of carrier concentrations and mobilities. First principles studies of defects in CdTe [15] have given valuable information about the expected level of carrier concentration for different doping elements or defect concentration. On the other hand, doping wide band gap compounds has been observed to be more difficult probably because of the presence of defect levels into the band gap, inducing compensation (carrier killers) [16].

1.3.5 Nanostructures

An important advantage of II-VI compounds is the capability to form nanostructures by simple preparation procedures. For small sizes, the quantum confinement effect allows for the modification of the band gap as a function of size. But, even at larger sizes, these nanostructures are single crystals with a very low defect density and high surface to volume ratio. These properties make them very promising to fabricate detectors and other devices in different wavelength ranges with innovative designs [17]. Nanocrystals have been fabricated using both top-down and bottom-up techniques. In the first variant, bulk materials are fractioned in small pieces with sizes smaller than around 100 nm by using different techniques as electron beam lithography, focused ion beam, exfoliation, ball milling, etc. Better quality/smaller size nanocrystals can be obtained by the bottom-up approach. For example, different bottom-up (both dry and wet) chemical methods have allowed to obtain nanocrystals of all II-VI compounds with excellent properties. When the size of the nanocrystals become smaller than the exciton Bohr ratio, circa 5–6 nm, quantum confinement results in the apparition of discrete energy levels whose position depends on the nanocrystal sizes. These objects are called quantum dots (QDs) and present unique properties like size dependent band gap, strong luminescence, large absorption coefficient, and narrow/broad emission/excitation spectrum. To enhance the luminescence properties of the QDs, different kinds of core/shell structures have been fabricated. For example, in the case of CdSe/ZnS core/shell dot, a widely studied structure, the larger band gap ZnS with similar bond length than CdSe is used to passivate the core surface leading to an important enhancing of the luminescence while also contribute to isolate the toxic elements of the core from the environment. Intense research work is now focused on the modification of the QDs surfaces to promote hydrophilicity and stability in the biological environments and to conjugate them with biomolecules of interest for targeting.

1.4 Applications

1.4.1 Infrared Detectors and Focal Plane Arrays

The mix of CdTe and HgTe produces the alloy $Hg_{1-x}Cd_xTe$ (also known as MCT) which was discovered in 1959 and is probably the flag ship of II-VI semiconductor materials. Depending on the composition x, the band gap of the alloy can be tuned to cover the needs of infrared detection and imaging in all the characteristic infrared windows: short-wave (1–3 μm), mid-wave (3–5 μm), long-wave (8–14 μm), and very-long-wave (14–30 μm). Individual detectors on both photovoltaic and photoconductive modes and focal plane arrays (FPA) are today fabricated using liquid phase epitaxy or vapor phase nonequilibrium techniques like molecular beam epitaxy (MBE) or metal organic vapor phase epitaxy (MOVPE) [13]. Compared with III-V materials competitors like InSb/GaSb type II superlattices, for example, MCT devices present much better performance due to its high quantum efficiency and larger minority carriers lifetime. Recent developments and challenges in $Hg_{1-x}Cd_xTe$ IR FPA for military, civilian, medical, and industrial applications like night vision, reconnaissance, surveillance, missile guidance, remote sensing, firefighting, security, pollution-monitoring, leak-testing, thermography, and cancer and tumor detection are described in a relatively recent review [18]. Present trends in FPA are focusing in decreasing the pixel size and the power consumption and to increase the area, operating temperature, frame rates, and thermal resolution. $Hg_{1-x}Cd_xTe$ is today the indisputable leader in IR detection and imaging despite the disadvantage related with the toxicity of their components.

1.4.2 Devices in the THz Range

An interesting range of the electromagnetic spectra is the so-called submillimeter or THz range which goes from some tenths to a few tens of THz or equivalently for wavelengths between circa 100–1000 μm, which partially overlap the far IR region. In this range, in between microwave and optical technologies, electromagnetic waves are strongly absorbed by water and metals while are penetrating in other materials as plastics and textiles. These properties together with the fact of being a nonionizing radiation has promoted the use of this electromagnetic range for several applications as nondestructive imaging, communications, or molecular spectroscopies. II-VI materials are important protagonist in this research area, too. The high nonlinear electro-optical coefficient of some II-VI semiconductors like ZnTe [19, 20] and CdTe [21] makes them materials of first choice for the generation of pulses with a broadband spectra in the range of 0.1–3 THz, using the optical rectification of femtosecond laser pulses (Ti or Yb lasers).

HgCdTe inter-band lasers are also promising in the range 5–15 THz in which quantum cascade III-V lasers fail because their emission is absorbed by the lattice [22], while the lower phonon energies of HgCdTe avoid lattice absorption. In contrast, the main problem stopping with HgCdTe stimulated emission is the strong Auger recombination rate in this material. Unique properties of HgCdTe as the existence of Dirac semimetal or topological insulator states can be useful for THz emission or detection mainly due to the high mobility of the carriers in these “exotic” states. In [22], the authors have demonstrated both detection and imaging with radiation of some tenths of THz as well as stimulated emission in the range 20–60 THz range.

1.4.3 X-Ray and Gamma Ray Detectors

The combination of a relatively large band gap and high atomic number of its component elements (48 and 52 for Cd and Te, respectively), CdTe and $Cd_{1-x}Zn_xTe$, are widely used as X-rays or gamma rays detectors [23]. They are particularly important in the range of high-energy photons, where silicon, germanium, or GaAs detectors have very large attenuation lengths. In fact, CdTe is one of the so-called high Z materials with good energy resolution and sensitivity. Typically, the $Cd_{1-x}Zn_xTe$ alloy with x ranging from 0.08 to 0.15 has an increased band gap with respect to CdTe which leads to lower leakage currents and better resolution in spectroscopic applications. These kinds of detectors are relatively large and are fabricated from bulk single crystals. They are widely used in medical imaging [24] and security inspections.

Today, there are commercially available cardiac image devices based on CdZnTe. These devices have been observed to increase sensitivity, contrast, and resolution with respect to scintillation based ones, this leading to an increase of the diagnostic confidence and reduced radiation exposure [25, 26]. Energy-resolved photon counters of CdZnTe, including spectroscopic features to better resolve the images details, have provided enhanced contrast in digital mammography for detecting breath tumors [27]. New generation of gamma cameras with increased spatial and energy resolution is using pixelated CdZnTe material [28]. Hard X-rays and gamma rays CdTe and CdZnTe detectors, associated with different kinds of telescopes, are widely used in the exploration of the universe [24].

1.4.4 Solar Cells, UV-VIS Detectors, and Light-Emitting Devices

In the visible range, CdTe is also a very renowned compound. As well as its III-V partner GaAs, CdTe possesses a band gap of 1.4 eV which is near to the optimal value for a solar cell absorber material. This has given rise to the development of polycrystalline thin films solar cells based in CdTe which has reached more than 20% of efficiency [29, 30]. They have been prepared by using several techniques as close space vapor transport, thermal evaporation, chemical bath deposition, or sputtering. On the other hand, CdS, ZnO, and ZnS, with larger band gaps, are frequently used as window partners of CdTe or other absorber-based solar cells. Other II-VI semiconductors as ZnTe or HgTe are often used to achieve ohmic contacts to the moderately p-type CdTe [31].

CdS nanowires, traditionally used in UV/blue detection, have been proposed to integrate multicolor detectors in combination with diamond, InGaN, or ZnO [32]. Taking advantage of the ZnS large band gap, ZnS nanobelts [33] have been used for UV "solar blind" detectors, while CdS photodetector arrays have been prepared in flexible polyethylene terephthalate (PET) substrates [34], and individual ZnSe nanobelt has been used as UV photodetector [35].

In the late 1980s and early 1990s, intense research efforts on ZnSe and related alloys were devoted to the fabrication of blue light-emitting devices, but these efforts were truncated because of the impressive development and success of GaN-based devices. However, laser research has become an important research topic again in II-VI semiconductors, now in the MID IR range. Transition metals or rare earth doped II-VI semiconductor presents tunable wideband laser emission. For example, optically pumped (using Tm or Er fiber lasers, or directly with diode lasers) Cr or Fe doped ZnS and ZnSe lasers have been fabricated [36, 37]. Depending on the used configuration, the laser emission can be tunable in the range of 1–3 μm. They are used in several applications as remote sensing, environmental monitoring, mid-IR communications, optical coherence tomography, ophthalmology, and dermatology [38, 39].

An important contribution of II-VI materials is in the field of phosphors. Sulfides are among the first discovered phosphor materials. ZnS, whose luminescence was discovered in 1866, has been recognized as the most important phosphor material matrix [40]. Alternated current-driven electroluminescence (ACEL) is the preferred configuration in these devices. In particular, ACEL powder-based devices [41], in which luminescent particles are embedded in a dielectric binder, allow large area and colored light sources by simple screen printing techniques when using ZnS:Cu (other dopants such as Al, Cl, Mn, Ag, etc. can be used to change the emission wavelength in the range 450–690 nm; white emission has been reported using Eu as the dopant [42]). In another variant (ACTFEL), thin films of the phosphor elements are sandwiched between insulator films, and metal electrodes are deposited in both sides. In this conditions, electron tunneling from interface states to the phosphor film and impact ionization are responsible for light emission during AC cycles [43]. Displays with this technology are used in some applications due to advantages as large lifetimes, ease of manufacture, large viewing angle, and wide range of operating temperatures, among others.

On the other hand, II-VI QDs have shown excellent luminescent properties and can be used in a wide range of applications including luminescent biomarkers, light-emitting diodes, and lasers. The application of these QDs in biosensor will be the subject of the following paragraph.

1.4.5 Biosensors

II-VI QDs have found interesting biomedical applications including in vivo or in vitro chemical sensing, biomolecules targeting, luminescence imaging, and drug delivery [44]. They have demonstrated superior properties than traditionally used organic fluorophores [45]. For example, (i) QDs have a broad absorption wavelength range which allows excitation well above the emission region and makes possible to excite, with the same source, QDs emitting at different wavelengths; (ii) they have very intense luminescence, and due to the quantum 3D confinement of electron and holes, the emission wavelength can be controlled through the size; and (iii) they are resistant to photobleaching and are in general more stable than fluorophores. For sensing, the modification of the emission wavelength or intensity in the presence of specific biomolecules is used.

QDs are generally presented in a colloidal form in organic solvents, and Cd chalcogenides are probably the most studied colloidal QDs. To be used in biological media, QDs must be hydrophilic, but after their synthesis process in organic reactants, they result with hydrophobic surfaces. In fact, the first two demonstrations of QDs ability for bio-sensing [46, 47], using CdSe/ZnS and CdSe/CdS core/shell structures, respectively, were presented once the authors implemented procedures to hydrophilize the QDs and reached to conjugate biomolecules to their surfaces. After those pioneering work, several II-VI QDs have been widely used in bio-applications. A survey of the QDs-based biosensors in the period 2013–2018 [48] included 28 sensors based on II-VI compounds or alloys as CdTe, CdS, CdS_xSe_{1-x}, CdSe, and ZnS for a long list of targets including DNA, HIV, cancer cells, glycoproteins, dopamine, cardiac troponin, etc.

QDs biosensor research is a very active field since some challenges remain. One of them, the toxicity of Cd, a component element in almost all QDs for biological applications. Visible light-emitting QDs can only be limitedly used for in vivo biological imaging because of the high absorption of tissues in the visible range. Then near-infrared (NIR) emitter composed of III-V InAs or IV–VI PbS is commonly used. Even in these cases, II-VI materials as ZnS or CdZnS are used as shells.

1.4.6 Gas Sensors

Traditionally, gas sensor devices have been dominated by metal oxide materials. However, semiconductor chalcogenides have been considered to be attractive in this area [50] after the demonstration of sensitivity, selectivity, and fast response/recovery in gas sensing at RT. For example, CdS QDs/Co_3O_4 composites have shown high sensitivity and low response and recovery times for H_2S sensing at room temperature [51]. CdSe QDs/ZnO composites have shown sensitivity toward NO_2 under green light illumination [52]. The authors ascribe the effect to the transport of photogenerated electrons from the CdSe to the ZnO which influence the interface potential and the adsorption desorption process of NO_2.

1.4.7 Photocatalysis

In semiconductor photocatalytic technology, solar energy is used to promote chemical reactions. Typical examples of photocatalytic process are the production of H_2 fuel by the splitting of water, or the degradation of toxic contaminants, both with obvious implications in energy and environmental matters. The conventional TiO_2 catalytic material with a band gap of 3.2 eV wastes most of the solar energy spectra. For this reason, other semiconductors with lower band gaps have been tested as photocatalysts; this is the case of some II-VI semiconductor-related materials. With a band gap of 2.4 eV and excellent electrical conductivity parameters, CdS has been considered a significant candidate [53]. In fact, H_2 evolution has been demonstrated using CdS with different morphologies as nanowires, QDs, or hollows structures, among others. To resolve instability of CdS chemical properties or photo-corrosion effects, different kinds of composites have been used as, for example (among many others), TiO_2/CdS [54, 55] or n-doped graphene/CdS [56], with enhanced catalytic efficiencies. CdS catalytic properties have been also used to reduce the CO_2. a greenhouse and contaminant gas to clean hydrocarbon fuels such as CH_4. In this case, the requirement of cocatalysts is more needed, and several composites have been used; for example, reduced graphene oxide–CdS nanorod composite has shown excellent catalytic efficiencies [57]. On the other hand, the porous CdTe QDs/NTU-9 metalorganic framework nanocomposite has demonstrated rapid photodegradation of rhodamine 6G, a polluted dye [58], while CdSe nanoribbons have been used as photocatalyst hydrogen production from water in the presence of Na_2S/Na_2SO_3 as sacrificial electron donors under UV and visible light [59].

1.5 Conclusions and Outlook

II-VI compounds, with a very early presence in the history of materials and being founders of the semiconductor science and technology, represent today an active research and development area. Some examples of devices and structures developed on the basis of II-VI compounds are shown in Fig. 1.3.

Several semiconductor industries use II-VI compounds or alloys, many laboratories around the world are involved in II-VI compounds research and development, and many public or private agencies devote a lot of resources for the study of this kind of materials with the purpose of making new more efficient devices. In detector technology relays most of the importance of II-VI compounds. HgCdTe and CdZnTe are excellent examples in IR and gamma/X-ray detection. Novel nanostructures as nanocrystals, quantum dots, quantum well, or nanowires have demonstrated their possibilities and potentialities in several applications.

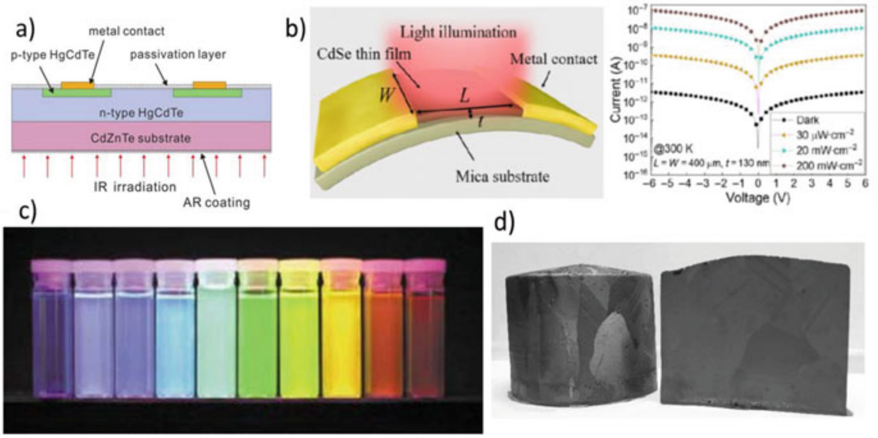

Fig. 1.3 Illustration of some kinds of detectors based in II-VI materials. (**a**) Planar structure of a p-n HgCdTe IR photodiode detector. Reproduced with permission from Ref. [13]. Copyright 2015: AIP Publishing; (**b**) schematics of a CdSe/mica flexible photodetector and its dark and illuminated I–V characteristics. Reproduced with permission from Ref. [60]. Copyright 2022: Springer; (**c**) Ten distinguishable emission colors of ZnS-capped CdSe QDs excited with a near-UV lamp. Reproduced with permission from Ref. [49]. Copyright 2001: Springer; (**d**) 8 in (24 kg) CZT ingot grown by the HP-EDG technique at eV Products, Inc. from which X-ray and gamma ray detectors are fabricated. Reproduced with permission from Ref. [61]. Copyright 2018: AIP Publishing

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