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Introduction

As an important branch of research in two-dimensional semiconductor materials, chalcogenides have unique properties, diverse crystal structures, strong light–matter interactions, high carrier mobility, and other advantages. These excellent characteristics also make them candidate materials for solar cells, sensors, photodetectors, and other devices, which have aroused great research interest in the past few decades.

In this chapter, we define chalcogenide semiconductors and provide an overview of their historical development. The focus will be on the key properties, along with their applications across communication, sensing, and storage sectors. Through these introductions, the infinite potential of chalcogenide semiconductors in advancing electronic device technology is highlighted.

1.1 Definition of Chalcogenide Semiconductors

1.1.1 Basic Definition of Chalcogenide Semiconductors

Chalcogenide semiconductors are materials containing one or more chalcogen elements (sulfur, selenium, or tellurium) combined with other elements like metals or metalloids (e.g., germanium or arsenic). Their unique chemical and physical properties give them broad application prospects in semiconductor materials. These materials can usually be synthesized by simple chemical reactions or physical methods to form a wide range of crystal structures and morphologies. The main advantage of chalcogenide semiconductors is their excellent optoelectronic properties, including large nonlinear optical response, tunable bandgap, and good thermal stability. These properties enable them to show great potential for applications in nanophotonics, optical communications, optical storage, and other fields (Figure 1.1).

Since the beginning of the 20th century, chalcogenide semiconductors have gradually received attention from the scientific community. Early research mainly focused on the underlying physical properties of these materials. As technology advances, research is increasingly focusing on its performance in practical applications, particularly in the field of nanophotonics. Chalcogenide semiconductors have garnered attention due to their adjustable optical bandgap and high refractive index.

Chalcogenide Nanophotonics, First Edition. Tun Cao, Ying Su, Yinghan Li, and Hongze Gao.

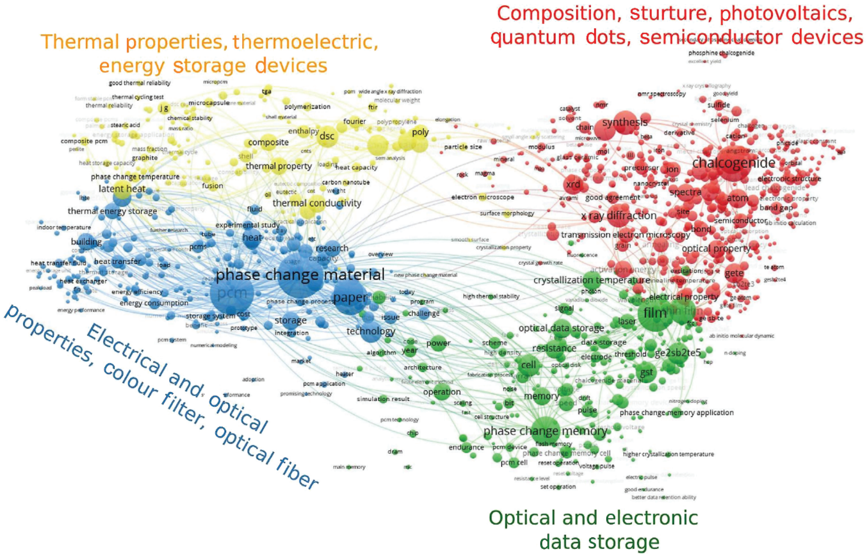

Figure 1.1 Semantic assessment of abstracts from the ISI Web of Science using the key word "chalcogenide". *Source:* Adapted from Cao et al. (2020).

Through bandgap engineering and phase transition modulation, these materials can realize the modulation of optical properties on a microscopic scale, which fully meets the special requirements of materials for modern optoelectronic devices. As an example, germanium-sulfur (GeS), a compound of germanium and sulfur, is a typical chalcogenide semiconductor with a low-energy bandgap suitable for photovoltaic conversion in the visible and infrared wavelengths. The composition of chalcogenides can be optimized by changing the ratio of metal elements to chalcogenides and by introducing other doping elements. This component modulation capability allows design flexibility for chalcogenides in optoelectronic devices. For example, lead sulfide (PbS), as an important narrow bandgap semiconductor material with excellent photoconductivity and thermoelectric properties, is widely used in fields such as photodetectors and thermoelectric converters. With the deepening of research, more and more novel ternary or quaternary sulfur compounds have been discovered, such as bismuth selenium (Bi_2Se_3) and bismuth alloy selenium ($Bi_2(SeTe)_3$). Chalcogenide materials possess excellent optical and nonstructural properties, making them applicable in emerging fields such as topological insulators and photoelectrocatalysis. Their complex composition lays a crucial foundation for investigating phase transitions, superconductivity, and nonlinear optical properties. Consequently, the study of chalcogenide semiconductors has become a significant area of focus in materials science and optoelectronic engineering.

In recent years, significant progress has been made in related research as methods for synthesizing chalcogenide semiconductors continue to mature. Currently, researchers have successfully applied chalcogenide semiconductors in a variety of optoelectronic devices, including optical switches, optical storage devices, and fiber-optic communication systems. Chalcogenide semiconductors have demonstrated excellent performance in cutting-edge applications such as optical field modulation and optical signal processing. Through an in-depth study of chalcogenide semiconductors, we can better understand their unique physicochemical properties and thus promote further development of related technologies.

1.1.2 Classification of Chalcogenides

Chalcogenides are compounds that have sulfur elements (e.g., sulfur, selenium, and tellurium) as their main components and are widely used in semiconductors, optoelectronic materials, and various types of new functional materials.

According to the valence state, chalcogenides can be roughly divided into the following categories: first, binary chalcogenides, such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2); second, ternary and multivariate chalcogenides, which contain not only sulfur but also other elements such as gallium, and indium, such as the ternary tin sulfide ($Sn_1{-}_xGe_xS$) and multivariate rare-earth sulfur compounds (RE_2S_3), which tend to have more complex structures and a wealth of physical properties. Among binary chalcogenides, the most common are transition metal disulfides (TMDs), which usually have a layered structure and can be prepared by mechanical stripping or chemical vapor deposition, etc., as single- or few-layer materials that exhibit excellent optoelectronic properties. For example, MoS_2, as a typical TMD, has become an important research object in the field of 2D materials due to its direct bandgap properties. WSe_2, on the other hand, implies excellent spin properties. In these materials, the interlayer interactions are relatively weak, allowing them to exhibit a wealth of physical phenomena such as superconductivity and photoconductivity when externally modulated. Ternary and multivariate chalcogenides have superior properties due to their compositional diversity. For example, Ge–Sb–Te system materials (GSTs) have been widely studied and applied in phase change memories, where they exhibit significant optical changes during the phase change process, enabling fast data access. Such alloys can also achieve bandgap modulation by adjusting the composition ratio, which provides new ideas for device performance optimization. Low-dimensional ternary chalcogenides are also gaining attention for thermoelectric, catalytic, and photodetector applications, where they typically exhibit high carrier mobility and excellent thermoelectric properties.

Chalcogenides can be classified into metal, nonmetallic, alloy, and composite chalcogenides based on their composition and structure. Metal chalcogenides, such as lead sulfide (PbS) and cadmium selenide (CdSe), typically exhibit excellent optoelectronic properties and superior conductivity and are widely used in optoelectronic devices and sensors. Nonmetallic sulfur compounds, such as hydrogen sulfide (H_2S) and boron sulfide (B_2S_3), excel in areas such as catalysis, gas sensing, and environmental monitoring. In addition, the study of alloy and composite chalcogenides provides a wide scope for the design of novel materials, such as modulating the electronic and optical properties of materials by changing the ratio of different compositions.

According to the crystal structure, chalcogenides can also be categorized into glassy and crystalline states. Glassy chalcogenides, including germanium sulfide

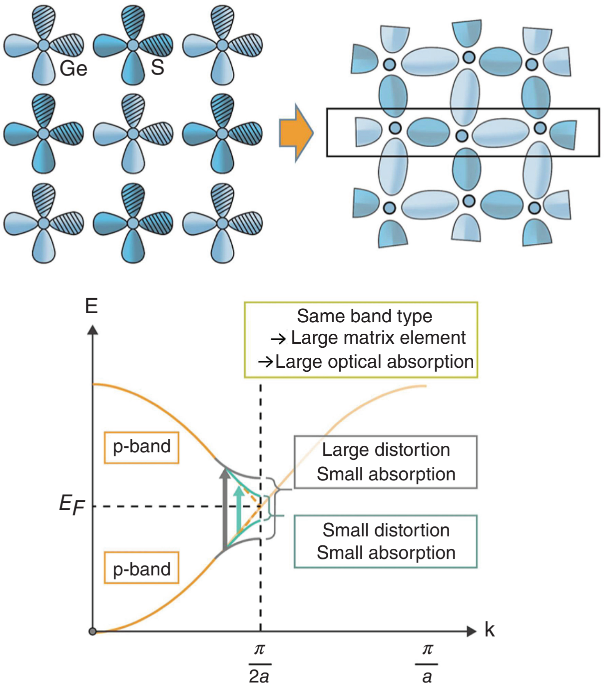

Figure 1.2 Visualization of bonding mechanisms in GeS and their impact on the electronic band structure. The upper section illustrates the atomic orbitals of Ge and S involved in bonding. σ-Bonds arise from overlapping p-orbitals, each occupied by approximately half an electron pair (ES ≈ 1), leading to a metallic band (represented by blue curves in the lower portion). Nevertheless, slight charge redistribution and/or minor Peierls distortions can induce a narrow bandgap.

(GeS) and arsenic sulfide (As_2S_3), as seen in Figure 1.2, are ideal for optical communication and storage devices because of their amorphous nature, which provides high optical transparency and nonlinear optical properties. In contrast, crystalline chalcogenides such as Sb_2S_3 and $Ge_2Sb_2Te_5$ exhibit exceptional optical and electronic properties due to their highly ordered structures. In nanophotonic applications, the phase transition and tunability of these materials make them key materials in novel photonic devices. For example, $Ge_2Sb_2Te_5$, as a phase-change material (PCM), can realize fast switching between solid and liquid states under different temperature and light conditions, providing the basis for high-performance memory and information processing devices.

Chalcogenides can be classified into various functional materials based on their application. These include photovoltaic materials, thermoelectric materials, photocatalysts, and more. For instance, chalcogenides used as photovoltaic materials have shown outstanding performance in solar cells and photodetectors, making them widely utilized in new energy technologies. Chalcogenides, such as bismuth selenide (Bi_2Se_3), are significant thermoelectric materials with vital applications in power generation and refrigeration due to their high thermoelectric efficiency.

Additionally, photocatalysts play an essential role in environmental remediation and energy conversion by facilitating chemical reactions using sunlight or other light sources, which helps achieve environmental purification and clean energy production. These categories provide a solid foundation for researching and developing new chalcogenides, paving the way for their applications in advanced fields such as nanophotonics.

In the realm of materials science and nanophotonics, chalcogenide semiconductors are of great importance due to their varied structures and extensive physical properties. A deeper exploration of the characterization and synthesis of different sulfur compounds, as well as the fundamental physical mechanisms behind them, is crucial for a more comprehensive grasp of their features and possible applications.

1.2 Basic Properties of Chalcogenide Semiconductors

1.2.1 Chemical Properties

Chalcogenides are compounds based on sulfur, selenium, tellurium, etc., which usually combine with other metal or semimetal elements to form diverse structures. These compounds are widely found in nature and have many chemical properties covering a wide range of aspects from atomic structure to chemical reactions. The stability and reactivity of chalcogenides are influenced by their chemical composition, crystal structure, and synthesis conditions. Many chalcogenide semiconductors demonstrate exceptional thermal stability and oxidation resistance under high temperatures and pressures, providing a theoretical foundation for their use in extreme environments. The reaction rate and mechanism of such materials can be optimized by adjusting the type or proportion of metals to meet the needs of industrial applications. The synthesis methods of chalcogenides, including solid-state reactions, solution methods, and vapor-phase deposition methods, provide multiple avenues to further enhance their properties. These chemical properties make chalcogenide semiconductors show great promise for future applications in nanotechnology research.

1.2.2 Physical Properties

The structural forms of chalcogenides—both amorphous and crystalline—play a crucial role in materials research, influencing not just their optoelectronic behavior but also offering distinct benefits across multiple applications.

Glassy chalcogenides are usually disordered during cooling and exhibit excellent nonlinear optical properties, making them suitable for fields such as optical communications and optical storage. In the glassy state, chalcogenides not only maintain high flexibility and plasticity but also have good optical transparency, which makes them have broad prospects in optical coatings and fiber applications.

Chalcogenides can form a variety of crystal structures, including cubic, hexagonal, and orthorhombic systems. These crystals typically exhibit high thermal conductivity and excellent electrical conductivity, which has led to increased interest in their use as thermoelectric materials. Specific chalcogenides, such as GeTe and Sb_2S_3, undergo phase changes at certain temperatures and pressures, significantly influencing their light response properties. The different crystal morphologies affect the bandgap and other optical properties of the material, which are essential for developing efficient optoelectronic devices. Additionally, structural changes during phase transitions enable these materials to display novel physical properties on the nanoscale, including the formation of defect states and the excitation of localized surface plasmon resonances (LSPR).

The mutual transformation between the glass and crystal morphology of chalcogenides is also an important research direction. By adjusting the temperature, pressure, and chemical composition, scientists can achieve a reversible transition from the crystalline to the glassy state. This transition affects the physical and chemical properties of the material, such as thermal conductivity and optical properties, and is therefore essential for understanding and utilizing the properties of sulfur compounds. In recent years, it has been shown that suitable doping and modulation can significantly increase the glass transition temperature and stability of chalcogenides, thus expanding their potential for applications in nanophotonics. Understanding the properties of glass and crystal forms of chalcogenides will provide a theoretical basis for the design and optimization of new materials and promote their further development in modern technology.

With the deepening of the research, the thermodynamic properties, photoelectric properties, and surface plasmon resonance of chalcogenides have been gradually revealed, which provides a theoretical basis for their expansion in different application fields. Especially for sensors and optical storage devices, chalcogenides are important candidates for emerging nano-optoelectronic devices due to their strong light absorption in specific wavelength bands and excellent electrical properties. By precisely controlling the physical properties of materials, scientists can develop more efficient and multifunctional optoelectronic devices to meet the growing market demand and technological challenges.

1.2.3 Optical Properties

Chalcogenides have garnered significant attention due to their unique optical properties, which show great potential for applications in nanophotonics. These materials are particularly notable for their nonlinear optical characteristics, enabling responses such as second harmonic generation (SHG) and self-focusing phenomena when subjected to external excitation. The nonlinear effects arise from their complex crystal structures and chemical compositions, making chalcogenides important in fields like optical frequency conversion and optical signal processing. The bandgap of chalcogenides can be tuned by altering the material's composition and structure. This bandgap engineering not only broadens their applications across a wide range of wavelengths but also allows for excellent light absorption and emission properties at specific wavelengths. The nonlinear optical properties and bandgap engineering of chalcogenide semiconductors will be explored in detail later.

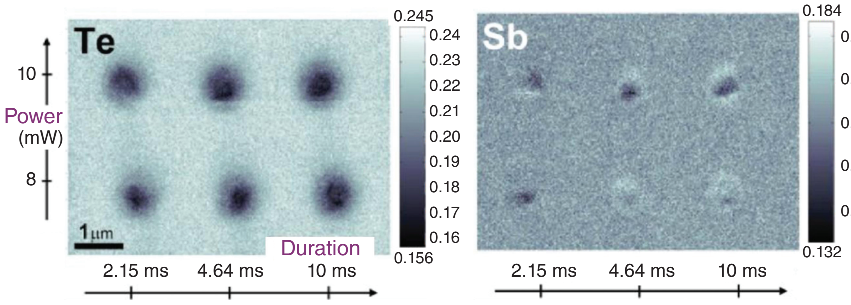

Figure 1.3 Auger electron spectroscopy with high resolution applied to Te-enriched GST during laser-driven crystallization. *Source:* Debunne et al. (2011) / IOP Publishing.

The phase transition behavior in chalcogenides also significantly affects their optical properties. When utilizing PCMs for photonics applications, chalcogenides can rapidly transition between different crystalline states, which in turn changes their optical refractive index. This feature provides a new implementation approach for optical storage, optical switches, and optical modulators. $Ge_2Sb_2Te_5$, for example, exhibits extremely high reflectance or transmittance variations during the phase transition process, which greatly enhances its applicability in optoelectronic devices. The high transparency and low optical loss of chalcogenides make them suitable for use in the manufacture of high-performance optical waveguides and optical fibers (Figure 1.3).

The crystal morphology (glassy and crystalline) of chalcogenides also has a significant impact on their optical properties. In the glassy state, chalcogenides typically have a wider spectral range and higher transparency, while in the crystalline state, their optical properties are affected by crystal orientation and defects, thus placing higher demands on the preparation process of the materials. By regulating the preparation conditions, chalcogenides with excellent optical properties can be obtained, thus promoting the realization and application of photonics-related technologies.

Chalcogenide semiconductors have garnered significant interest in nanophotonics owing to their exceptional nonlinear optical characteristics. These properties arise when a material's interaction with light depends nonlinearly on the incident intensity, typically scaling quadratically or beyond. In chalcogenides, such behavior originates from their large nonlinear optical susceptibilities and adjustable bandgaps, which position them as promising candidates for advanced optoelectronic applications. The nonlinear response of these materials relies on their unique crystal structures and chemical compositions, allowing them to exhibit several excellent properties in the field of optics. For example, binary or multivariate chalcogenides, such as GeTe and Sb_2S_3, can be tuned by adjusting the ratios of the constituent elements and the external conditions (e.g., temperature and pressure) to achieve the modulation of their nonlinear optical properties. This flexibility makes chalcogenides potentially practical in applications such as laser technology, light modulation, and frequency conversion.

Research indicates that the nonlinear optical properties of chalcogenides mainly include optical SHG, self-focusing effects, and optical switching effects. Optical SHG refers to the phenomenon where the frequency of light waves is doubled in a material when exposed to high light intensities. Many chalcogenides exhibit significant SHG effects, making them preferred materials for use in nonlinear optical devices. Owing to their large nonlinear refractive index and broad bandgap characteristics, chalcogenides show great potential for ultrafast optical pulse generation and control.

Notably, their nonlinear optical performance can be further improved by engineering subwavelength geometries and localized electronic states. In cavities, these materials exhibit strong optical nonlinear behavior, with potential mechanisms including multiphoton absorption, phase matching, and self-focusing phenomena. As an example, the nonlinear refractive index of chalcogenides increases significantly under intense laser irradiation, allowing for ultrafast optical switching and modulation. This phenomenon is attributed to the strong electron–phonon interactions in the material, as well as to the compounding and recombination processes in the excited states, which in turn lead to the enhancement of nonlinear optical effects. Therefore, these materials can find applications in lasers, ultrafast optics, and optical communications.

Utilizing the nonlinear optical properties of chalcogenides, the researchers have also developed novel perfect absorbers and optical filters. These devices enable efficient absorption and selective transmission of light at specific wavelengths, greatly improving the performance of photonic devices. For example, by employing structural modulation and chalcogenides of different compositions, it is possible to modulate the propagation characteristics of light in the design of the absorption peaks, thus realizing precise control of optical signals. With the in-depth study of the nonlinear optical properties of chalcogenides, the performance optimization and application prospects of these materials have been further expanded. For instance, recent studies have found that the nonlinear optical properties of these materials can be enhanced using different synthesis methods and post-processing techniques, thus broadening their application in modern photonic devices. These advancements not only enable performance optimization in optoelectronic devices but also offer viable pathways for implementing quantum computing architectures and photonic-integrated circuits. The demonstrated capabilities highlight chalcogenides' significant potential for nanophotonic applications, while establishing fundamental building blocks for next-generation ultrafast optical systems and advanced information processing platforms based on these materials.

Bandgap engineering involves the strategic modification of a material's composition, structure, or external parameters to achieve precise tuning of semiconductor bandgaps and their associated electronic properties. This technique is especially significant in chalcogenide semiconductors. The bandgap of chalcogenides is influenced not only by the elements that make up the material but also by factors such as crystal structure, orientation, and stress. By carefully regulating these parameters, it is possible to design the bandgap effectively.

The most common method in bandgap engineering is to change the constituent elements of the material. In the transition metal dichalcogenides MX_2, the bandgap properties can be significantly altered by substituting a different transition metal (M) or chalcogenide (X). For example, replacing rhenium (Re) in rhenium disulfide (ReS_2) with molybdenum (Mo) or tungsten (W) not only perturbs the atomic orbital interactions but also modifies the bandgap. Regulating the nonchemical composition of materials is an important approach, particularly in adjusting the number of layers present. The structure, whether it consists of single or multiple layers, has a significant impact on the bandgap of the material. For instance, single-layer MoS_2 acts as a direct bandgap semiconductor, while multilayer MoS_2 functions as an indirect bandgap semiconductor. Therefore, the bandgap can be precisely engineered through controlled modulation of material thickness and layer architecture.

In addition to the chemical composition and the number of layers, the engineering of the bandgap can be achieved equally well by the modulation of external conditions. Under high-pressure or low-temperature conditions, the bandgap of a material can change significantly due to stress- and temperature-induced changes in the crystal structure and adjustments in the electronic energy band structure. It has been found that under high pressure, certain sulfur compounds undergo a phase transition from semiconductors to metals and that the bandgap changes accompanying this phase transition allow them to exhibit different properties under different application conditions. Bandgap tuning through external stimuli (such as electric fields or optical excitation) enables dynamic control in photonic applications, particularly for optical modulators and high-speed switching devices. For example, by applying an electric field, the polarization of a material can be induced to modulate its energy band structure for rapidly controlling optical and conductive properties.

The research on the bandgap engineering not only improves the understanding of material properties but also provides a theoretical basis for the design of novel devices. In the field of optoelectronics and nanophotonics, the application of bandgap engineering has enabled these chalcogenide materials to exhibit good performance in optical communications, sensors, optical storage, and other areas. More importantly, developments in this area will drive future innovations in new, more efficient, and smarter optoelectronic devices. By further exploring the mechanisms involved in bandgap engineering, it will help to crack the limitations of the performance of existing materials and realize a wider range of material applications.

1.2.4 Optical Force

Optical forces refer to mechanical forces resulting from the interaction of light with matter, such as effects like optical tweezers and phototransformation. And the deformation mechanism of chalcogenide semiconductors under the action of optical forces is a hot spot of current research.

The main mechanisms of deformation of chalcogenide materials under optical forces include photo birefringence, optical torque, and photomobility. Photogenic birefringence is the phenomenon of birefringence that occurs when a material is exposed to light and stresses are generated within the material, resulting in a change in the refractive index. Light torque refers to the torque generated inside a material due to exposure to light, resulting in a rotational deformation of the material.

Photomobility means that light causes increased fluidity within the material, which results in deformation.

The application of chalcogenide semiconductors in optical force modulation is mainly based on their unique light–matter interaction mechanism and tunable optoelectronic properties. Taking phototropic phase transition–driven light field modulation as an example, chalcogenides (e.g., the Ge–Sb–Te system) can realize dynamic switching of refractive indices by amorphous–crystalline phase transitions in the presence of light. This characteristic, combined with the design of metasurfaces or photonic crystal microstructures, can generate a strong gradient electromagnetic field distribution in the local optical field, thereby inducing significant optical forces through the transfer of optical momentum. Reconfigurable optical tweezer systems developed with such materials enable subwavelength precision manipulation of nanoparticles. The lattice defects (e.g., sulfur vacancies) in two-dimensional transition metal chalcogenides (e.g., MoS_2, WS_2) significantly enhance the photoluminescence efficiency and amplify the light–matter interactions through the strong coupling of localized exciton states to the optical field. The local electromagnetic field intensity of defect sites may increase by more than 10 times, thereby enhancing the ability of optical forces to trap or drive micro- and nanostructures. In addition, photogenerated carriers generated by chalcogenide nanocrystals (e.g., Cu_2S–In_2S_3) in the presence of light can trigger lattice stress changes, leading to reversible deformations (e.g., bending or swelling) at the surface or interface of the material. This optomechanical coupling effect can directly convert light energy into mechanical displacement, providing a power source for optically driven actuators or microfluidic chips. Heterojunctions of chalcogenides (e.g., $Sb_{2-x}Bi_xS_3$) can dynamically adjust the direction and strength of the optical force by modulating the optical, thermal, and electrical multifield coupling. For example, in X-ray detection, the synergistic effect of photogenerated carriers and thermal expansion can optimize the sensitivity of the optical force in response to film deformation.

1.3 Application of Chalcogenide Semiconductors

1.3.1 Optical Communication

Optical communication technology is an advanced communication method that utilizes light as an information carrier for transmission, with significant advantages such as high speed, large capacity, and strong anti-interference ability. Chalcogenide semiconductors have shown their unique advantages in the field of optical communications, mainly due to their excellent optoelectronic properties and tunable bandgap. In recent years, the unprecedented growth in data transmission demands has revealed inherent limitations in conventional electronic communication systems, presenting critical scaling challenges. And optical communication has emerged as a key technology in addressing this issue, thanks to its high bandwidth and low latency. Chalcogenide materials, such as GeTe and Sb_2S_3, have unique advantages in this field due to their exceptional optical properties and tunable bandgap characteristics. These materials can effectively modulate their reflection, transmission, and absorption properties within specific wavelength ranges, enabling efficient modulation and demodulation of information transmission. Consequently, they can be utilized in the manufacture of essential devices, including optical modulators, optical switches, and optical waveguides.

Chalcogenide semiconductor materials offer new solutions to the challenges of conventional optical communication technologies in terms of spectral efficiency, transmission distance, and energy consumption. In optical communication systems, the application of chalcogenides is mainly reflected in their nonlinear optical properties and optical phase transition characteristics. The stimuli-responsive optical property modulation (temperature/pressure-dependent) in these materials significantly enhances gain while maintaining signal integrity during optical processing—essential characteristics for next-generation optical modulator design. For example, some chalcogenides undergo an insulator-to-metal transition during a phase transition, achieving effective switching of optical signals. In addition, by utilizing the phase transition properties of chalcogenides, efficient optical modulation can be achieved over a wider wavelength range, which means it can better adapt to the simultaneous transmission of multiple wavelength signals in optical communication systems. This characteristic makes them have great potential for application in high-speed optical communication, which can meet the bandwidth and speed requirements of future ultra-high-speed networks.

In addition, chalcogenide-based photodetectors offer significant sensitivity and range for optical communications. By adjusting the composition and structure of these materials, we can flexibly tune the bandgap, which allows for precise control of their optoelectronic properties. This enables efficient detection of optical signals at specific wavelengths. These enhancements not only improve the fidelity of information transmission and increase device compatibility but also broaden the application areas of optical communication networks, including fiber optic and wireless optical communications. In the future, as research on chalcogenide semiconductors deepens, we anticipate the development of more efficient and intelligent solutions for optical communications, further advancing communication technology.

1.3.2 Optical Storage

Optical storage technology, as an important part of the information storage field, relies on the optical properties of the material to realize the reading, writing, and storage of data. In the modern information society, with the explosive growth of data volume, traditional storage media face the double challenges of capacity and speed. Optical storage technology is gradually gaining attention due to its advantages of high density, high speed, and long-term stability. Chalcogenide semiconductors, as a new type of PCM, exhibit excellent optical properties and non-volatility, providing new possibilities for developing optical storage technology. These materials enable efficient modulation and storage of optical signals by changing their phase state, with advantages such as fast, reversible, and high-density storage. PCMs are characterized by their reversible structural transformations between distinct physical states under controlled external stimuli. A representative example is the laser-induced amorphous-to-crystalline phase transition, where the crystallization kinetics can be precisely modulated through optimization of laser parameters, including pulse duration and energy density. This controllable phase-switching behavior enables the development of non-volatile memory devices capable of reliable data storage operations.

Chalcogenide semiconductors, especially the Ge–Sb–Te (GST) series materials, are used in applications such as optical disks, photoresists, and high-performance two-dimensional materials due to their unique phase transition properties that give optical storage devices higher performance. These materials can rapidly change their crystal structure in the presence of light or an electric field, leading to the phenomenon of phase transitions, which enables the storage and reading of data. Laser irradiation can transform materials from an amorphous phase to a crystalline state, or vice versa, greatly improving the speed of data reading and writing. $Ge_2Sb_2Te_5$, for example, is a chalcogenide with excellent phase transition properties that is widely used in next-generation optical storage technologies. Due to its low-phase transition temperature, it can realize a fast-phase transition at room temperature, and thus the reaction speed in optical storage media is greatly improved. Thanks to their high thermal stability, chalcogenides exhibit excellent durability in information storage and are suitable for long-term storage applications, especially in optical discs, erasable optical discs, and flash memory technology. In addition, the tunability of chalcogenide semiconductors provides more scope for the design of optical storage devices. Researchers can optimize the optical properties of materials by changing their composition to meet the constantly increasing storage demands (Figure 1.4).

In recent years, the size of optical storage devices has been continuously reduced, greatly improving the density of data storage. Nanophotonic applications of chalcogenide semiconductors can further advance optical storage technology. Nanostructural modification provides an effective route to simultaneously engineer optical and electronic properties in functional materials, forming the physical basis for developing disruptive optical storage technologies. Through optical modulation technology, chalcogenide materials can realize reliable writing and reading of data in a shorter time, which effectively improves the response speed of the storage device. Although chalcogenides show promising applications in optical storage, they still face many challenges, such as material stability and durability. With further research, improving the stability, thermal conductivity, and light-absorbing ability of chalcogenide materials is expected to drive further development of optical storage technology. In the future, chalcogenide semiconductors will be more widely used in optical storage devices, providing strong support for the realization of faster and more efficient information storage.

1.3.3 Sensing Technology

The evolution of sensing technologies has enabled novel implementations of chalcogenide semiconductors, whose distinctive optoelectronic characteristics— including tunable bandgaps, pronounced thermo-optic effects, and phase-dependent

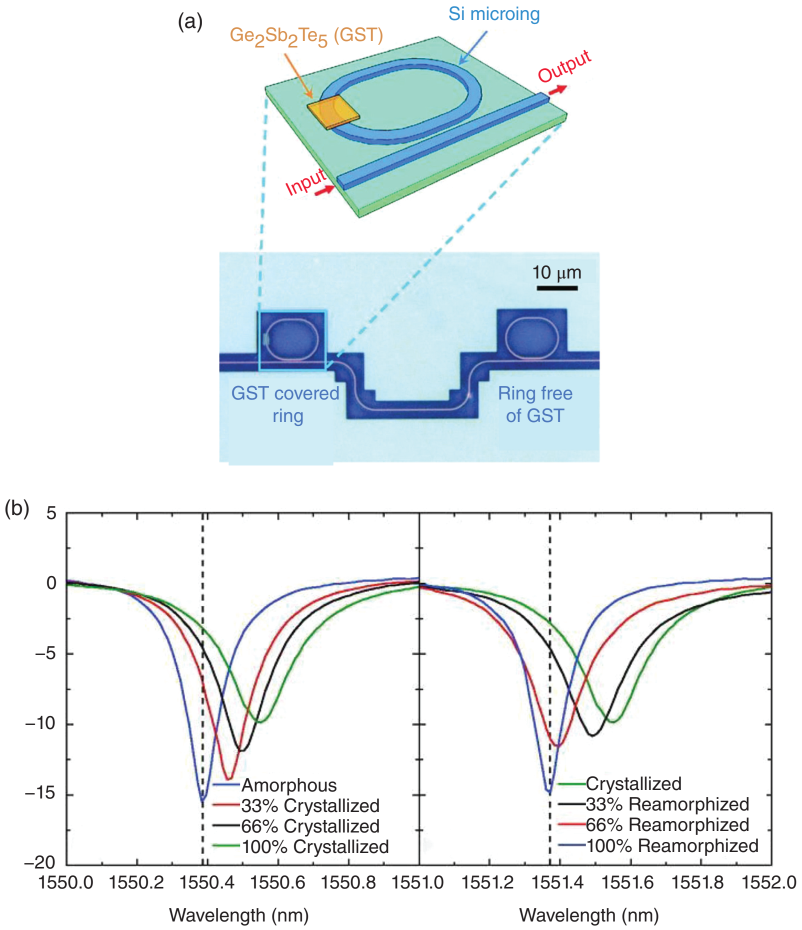

Figure 1.4 (a) A tunable photonic switch architecture comprising a Si racetrack resonator hybrid integrated with a $Ge_2Sb_2Te_5$ phase-change thin film, evanescently coupled to a Si waveguide. (b, c) Dynamically monitored transmission spectra demonstrating reversible optothermal switching characteristics during crystallization and reamorphization. *Source:* Rudé et al. (2013) / AIP Publishing LLC.

conductivity—make them ideal for advanced sensor designs. Nanophotonic engineering has particularly enhanced its detection capabilities, as evidenced by successful deployments in biochemical assays and ecological surveillance systems. The adjustable bandgap characteristics and nonlinear optical effects of these semiconductor materials give them superior sensitivity and response speed in low-concentration analysis and real-time monitoring processes. For example, two-dimensional chalcogenides such as molybdenum disulfide (MoS_2) and tungsten diselenide (WS_2) are widely used in gas sensors and biosensors due to their high mobility and excellent sensitivity.

Chalcogenide semiconductors have demonstrated exceptional performance in gas sensing. The selectivity and sensitivity to specific gases (e.g., ammonia, nitrogen dioxide, and ethanol) can be significantly improved by chemical modification of the material surface and construction of heterogeneous structures. The high specific surface area and excellent electrical conductivity of these materials make them ideal gas adsorption carriers, and the adsorption of gas molecules results in a change in the conductivity of the material, which enables the detection of gases. In many studies, modified sensors of MoS_2 and WS_2 have shown superior response and recovery times that are faster and more efficient than conventional semiconductor materials.

The applications of chalcogenides in biosensing are equally compelling. Using the biocompatibility and chemical modification capabilities of these materials, researchers have developed highly sensitive biosensors that enable real-time detection of biomolecules (e.g., DNA and proteins) by labeling them. The quantum dot optical properties of chalcogenides endow them with superior performance in optoelectronic sensing, enabling effective identification of target substances under low concentration conditions. These sensors not only have high sensitivity, which can significantly improve the signal-to-noise ratio and detection limit of the sensors, but also have high stability and repeatability, which can meet the stringent requirements in practical applications.

The contribution of chalcogenide semiconductors is also indispensable in the field of environmental monitoring. Utilizing its highly adjustable spectral response, researchers have developed a variety of sensors based on chalcogenide semiconductors for real-time monitoring of air quality, water pollution, and more. Chalcogenide semiconductors have demonstrated excellent flexibility and adaptability, especially in the detection of hazardous gases, which provides effective technical support in dealing with increasingly serious environmental problems. In short, the application prospects of chalcogenide semiconductors in the sensing field are broad, and they are expected to promote the emergence of more innovative sensors in the future, providing more accurate and efficient monitoring methods for various industries.

1.3.4 Other Applications

The applications of chalcogenide semiconductors in nanophotonics extend beyond conventional optical communications, data storage, and sensing systems. Their distinctive material characteristics facilitate diverse implementation possibilities across emerging technological frontiers. With the deepening of scientific research and the continuous development of related technologies, other applications of chalcogenides are gradually revealing their importance and market value. For example, in the field of chiral photonics, chalcogenide semiconductors also demonstrate enormous potential for applications. By constructing chiral nanostructures, chiral selective absorption and emission of light can be realized, which provides new ideas for the design of novel optical devices. In terms of achieving efficient chiral optical functionality, chalcogenide materials can optimize optical performance by adjusting their energy band structure on demand due to their bandgap engineering. This certainly offers more possibilities for realizing applications such as quantum communications, optical valves, and new laser sources.

Chalcogenide semiconductors have also received a lot of attention as excellent perfect absorbers. By modulating its microstructure and optical properties, it is possible to construct devices that can realize almost complete absorption of light of specific wavelengths, which are widely used in photothermal conversion, heat dissipation, and stealth technology. The design of such perfect absorbers not only improves the efficiency of energy utilization but also brings breakthroughs in areas such as photovoltaic conversion and energy storage. Some chalcogenide coatings can achieve nearly 100% light absorption efficiency across a wide spectral range, significantly enhancing the performance of photoelectric conversion devices. This advancement lays the groundwork for developing efficient photovoltaic equipment and infrared detectors. By combining sulfur compounds with other materials, it is possible to further improve their absorption properties. This approach can help meet the increasing demand for energy conversion and storage while also reducing production costs and material waste. In the future, these applications are expected to drive advancements in clean energy technology and contribute to sustainable development.

With the increasing demand for quantum computing and information processing, the prospect of chalcogenide semiconductors for applications in quantum optics cannot be underestimated. Based on its special electronic properties and tunable optical behavior, novel quantum information processing devices can be designed and developed. The performance of these devices depends on the quantum state manipulation of chalcogenides, which provides new solutions in areas such as quantum communication and quantum key distribution. It is expected to realize high-efficiency and low-energy consumption quantum computing platforms in the future, which will further promote the revolution in information technology and communication. The diverse applications of chalcogenide semiconductors are opening new directions and opportunities for the development of nanophotonics and materials science.

1.4 Research Progress of Chalcogenide Semiconductors

Owing to their special physical and chemical properties, chalcogenide semiconductors have shown great potential for applications in the field of nanophotonics, and numerous studies have been conducted around them.

On recent advances in chalcogenide semiconductors for nanophotonics, Tripathi et al. reviewed recent advancements in the chalcogenide PCMs in nanophotonics, covering various aspects from fundamental principles to practical applications, with focus on the advanced geometric engineering, the emergent functional capabilities, and the fundamental property modulation mechanisms governing light–matter interactions (Tripathi et al. 2023). Abdollahramezani et al. found that tunable nanophotonics can be achieved through chalcogenide PCMs. In the article, the authors provided an overview of the developments and trends in tunable metasurfaces and photonic integrated circuits using chalcogenide PCMs. The defining material properties, reversible structural transition processes, and pronounced thermo-optic coupling influence of widely studied categories of chalcogenide PCMs were outlined. Cen et al. (2019) provided an in-depth discussion on the fundamental principles and applications of phase transition material photonics of chalcogenides. Particularly, the developments of metal–chalcogenide–metal–trilayered plasmonic nanostructures are highlighted. The review pointed out the direction for the chalcogenide PCMs in growing areas of photonics. On the unique properties of semiconductors of chalcogenide semiconductors, Wuttig et al. revisited the correlations between the chemical bonding configurations and macroscopic properties, providing a theoretical basis for fundamentally optimizing the properties of the materials. Chew et al. focused on chalcogenide active photonics to provide new ideas for novel PCMs with enhanced spectral tunability across visible-to-near-infrared wavelengths through experimental and theoretical analysis. Martin-Monier et al. reviewed the durability of chalcogenide optical PCMs, discussed the factors influencing the crystallization and re-amorphization of several PCMs, examined their failure mechanisms, and formulated design rules for enhancing the cycling durability of these compounds. The review is critical for device stability and lifetime in practical applications.

In terms of related applications and preparation engineering, Cao et al. conducted a study on photonic GeSbTe phase transition metamaterials and their applications, revealing their unique advantages and potential application scenarios in the field of metamaterials. Piccinotti et al. optimized the properties of chalcogenide semiconductor alloys for nanophotonics applications by stoichiometrically engineering them to provide new strategies for material preparation.

The researchers have achieved remarkable results in the characterization of chalcogenide semiconductors and nanophotonic applications, and the multidimensional research from basic theory to practical applications has laid a solid foundation for the development of this field. However, there are still challenges, such as further optimization of material properties and expansion of new application areas, awaiting further exploration by researchers.

After understanding the history and conceptual framework of chalcogenide semiconductors and grasping their unique optoelectronic properties and relevance in modern photonics, the subsequent chapters of *Chalcogenide Nanophotonics* are structured to guide readers through a comprehensive progression from foundational principles to frontier innovations. Chapter 2 dissects electronic band theory, intrinsic material behaviors, and synthesis methodologies for chalcogenide thin films, providing critical insights for material optimization. Chapter 3 expands into deposition techniques, comparing chemical vapor deposition, thermal evaporation, and sputtering to address scalability and quality control. Chapter 4 transitions to optical phenomena, correlating macroscopic electrodynamics with advanced spectroscopic tools like Raman and emission spectroscopies. Chapters 5–8 pivot toward applied nanophotonics: optical communications (Chapter 5) analyze chalcogenide fibers and nonlinear effects; integrated photonic circuits (Chapter 6) explore memory devices and display technologies; photonic crystal platforms (Chapter 7) detail cavity and waveguide designs; and metamaterials (Chapter 8) showcase applications in optical switching, perfect lenses, and beam steering. By providing researchers with theoretical and practical strategies, we expect that chalcogenide semiconductors will occupy an increasingly important place in the future of nanophotonics.