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Introduction of Optical Imaging and Sensing: Materials, Devices, and Applications

Qimiao Chen[1]*, Hao Xu*[2]*, and Chuan S. Tan*[1]

[1] *Nanyang Technological University, School of Electrical and Electronic Engineering, Singapore 639798, Singapore*
[2] *University of Electronic Science and Technology of China, School of Physics, Chengdu 610054, China*

1.1 Optoelectronic Material Systems

Typically, optoelectronic devices for sensing and imaging can be fabricated by either group IV (Si, Ge, Sn, and their alloys) or compound semiconductors (like GaAs, InP, and GaN). Recently, there have been significant developments in on-chip integration using emerging two-dimensional (2D) materials and/or plasmonic structures to extend the wavelength range of silicon-based photodetectors beyond 1100 nm.

1.1.1 Si Platform

Si is not only the dominant material for the modern Information Age (also known as Silicon Age), which is driven by Si electronics, but also one of the most promising platforms for photonics to construct sensing or imaging systems. Si photonics, which is compatible with the current Si electronic industry, will share the benefits of Si technologies in terms of monolithic electronic–photonic integration, scaling, and low cost, which may result in a Si-based optoelectronic revolution in the future. Si photonics have been developed for various applications in the near-infrared (NIR) and shortwave infrared (SWIR) ranges.

Si photonics is a rapidly developing field. Recently, it has achieved a breakthrough with Ge-related materials (SiGeSn). As shown in Figure 1.1, the SiGeSn material system has some interesting optical properties that are ideal for constructing optoelectronic devices for sensing and imaging: (i) the lattice constant and bandgap can be tuned independently to form high-quality heterostructures to control the carriers; (ii) bandgap can be converted from indirect to direct; (iii) coverage of NIR, SWIR, and mid-infrared (MIR) wavelengths; (iv) the compatibility of growth temperature (<400 °C) with complementary metal oxide semiconductor (CMOS) process; and (v) high mobility, low Auger, and nonpolar.

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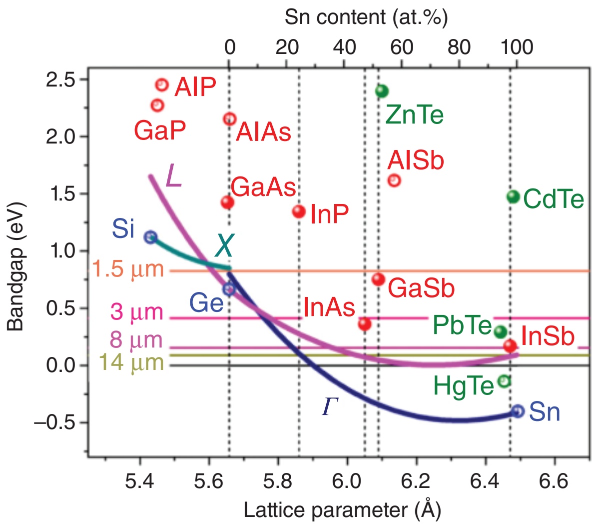

Figure 1.1 Bandgap versus of lattice constant of group IV, III–V and II–VI semiconductors. Source: Reproduced with permission from Moutanabbir et al. [1].

Early proposals to utilize SiGeSn materials for photonics date back to the 1990s. However, the actual development of practical devices has been hampered by the technical challenges of growing high-quality SiGeSn materials. While the thermal expansion coefficient mismatch between the epitaxial layer and Si substrates showed a positive effect on the epitaxial Ge layer, the large lattice mismatch between the elements (4.2% for Ge and Si, 14.7% for Sn and Ge, and 17% for Sn and Si) makes the grown layer tend to be defective and rough. For example, when the Ge or GeSn layer is epitaxially grown on Si substrates, misfit will inevitably be generated at the interface and propagate to the surface of the epitaxy layer as threading dislocations, which degrades the material quality and hinders the practical application of Ge or GeSn optoelectronic devices. Besides, it is challenging to incorporate Sn into Ge due to the extremely limited solid solubility of Sn (<1% in Ge), and Sn is prone to segregation at higher concentrations and growth temperatures. Therefore, GeSn alloys are unstable and require nonequilibrium growth. Fortunately, the device-level-quality SiGeSn materials have been grown recently by molecular beam epitaxy (MBE) or chemical vapor deposition (CVD) with various Ge and Sn precursors. We will introduce the growth of GeSn alloys and Ge by commercial CVD systems, which are of higher material quality and compatible with the industry for mass production.

To solve the first issue of lattice constant mismatch between epitaxial layers and Si substrates, relentless efforts have been made. Using a fully relaxed, thick-graded buffer layer can reduce the lattice constant mismatch between the Ge epitaxial layer and Si substrate. However, this method suffers from the issue of wafer bow as the graded buffer layer is usually too thick (~10 µm), so it could not be grown by industrial CVD tools. The second approach is the selective area growth (SAG) technique. The Si substrate is patterned, followed by epitaxial lateral overgrowth. Threading dislocations do not slide parallel to the growth direction, and they can slide to the window sidewalls and annihilate. The third more practical approach is the two-step growth method. A thin Ge seed layer was grown at low temperatures to restrict the mobility of Ge adatoms, thereby preventing 3D nucleation of Ge. Afterward, a thick Ge film is grown under high-temperature conditions for a higher growth rate and better Ge crystallinity.

For the growth of (Si)GeSn alloys, currently, the main Sn precursors are tetramethyl tin [$Sn(CH_3)_4$] and stannic chloride ($SnCl_4$). The main Ge precursors are GeH_4, Ge_2H_6, and Ge_3H_8. There are two approaches to obtaining GeSn layers with high Sn concentrations: (i) the spontaneous relaxation-enhanced (SRE) Sn incorporation process and (ii) the GeSn virtual substrate approach. When GeSn is grown on a Ge buffer using a fixed Sn concentration recipe, the Sn concentration will increase from the GeSn/Ge interface to the GeSn surface due to the strain relaxation. Thus, the grown layer will normally show two distinct layers, with the first strained layer being defective and the second relaxed layer having low defect density. Using the GeSn layer obtained by the SRE method as the virtual substrate to grow GeSn layers, an Sn concentration of up to 22.3% has been achieved. In addition to GeSn or Ge on Si substrates, some advanced engineered substrates, such as Ge(Sn) on insulator (GOI) and Ge on SiN (GON), have been proposed for the benefits of the smaller device area, increased packaging density, and high mobility.

Since the breakthrough in material growth, many devices have been developed for silicon photonics, including light emitters, amplifiers, photodetectors, waveguides, modulators, couplers, and switches. Progress has also been made in the most challenging components of Si light sources, and a complete set of components is being delivered for silicon photonics.

1.1.2 Two-dimensional Materials and Their van der Waals Heterostructures

Graphene was discovered in 2004 and the discoverers won the Nobel Prize due to its attractive 2D properties. Since then, many atomically thin 2D layered materials have been discovered, ranging from metallic (graphene and $TaSe_2$), semiconducting (WSe_2 and MoS_2), superconducting ($NbSe_2$ and FeSe) to topological insulators (Bi_2Se_3 and Sb_2Te_3). Through the combination of quantum confinement and enhanced electronic interactions, these atomically thin materials become strongly renormalized. Besides, different 2D materials can form various heterostructures by weak van der Waals forces. Figure 1.2 illustrates the available 2D materials and their electronic band structures covering a wide range of the electromagnetic spectra, from ultraviolet, visible, infrared to microwave, which would have different applications such as sensing, optical communication, and thermal imaging. We will introduce the properties of some typical individual 2D materials, followed by their van der Waals heterostructures.

1.1.2.1 Graphene

Graphene is a zero-gap semimetal with a single layer of 2D honeycomb carbon atoms. The resistivity will be reduced exponentially by adding electron/hole carriers. The interaction of the surrounding electrons around the honeycomb carbon atoms leads to the quasiparticles of massless Dirac fermions. Graphene has many

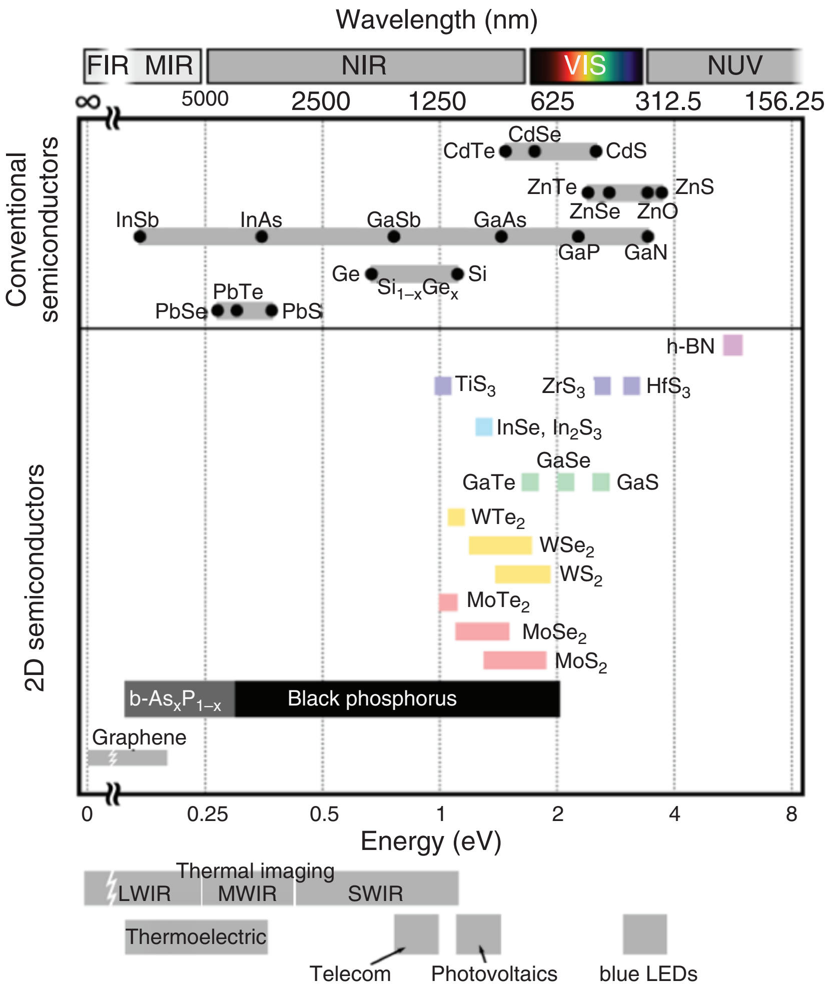

Figure 1.2 2D materials with potential applications in different wavelength regimes. Source: Reproduced with permission from Castellanos-Gomez [2].

attractive properties, such as high electron mobility (up to 2.5×10^5 cm^2 V^{-1} s^{-1}), high thermal conductivity (>3000 W mK^{-1}), high intrinsic strength of 130 GPa, and Young's modulus of 1 TPa.

1.1.2.2 Transition Metal Dichalcogenides

Transition metal dichalcogenides are atomically thin semiconductors with the formula MX2, with M, a transition metal element (Mo, W, or Nb), and X, a chalcogen element (S, Se, or Te). A pane of transition metal atoms is sandwiched by two layers of chalcogen atoms, as shown in Figure 1.3. The electrical and optical properties can be tuned by incorporating different transition metal elements. Transition metal dichalcogenides (TMDs) can vary from semiconducting to metallic characteristics, and some even demonstrate superconductivity characteristics (NbS_2 and $TaSe_2$).

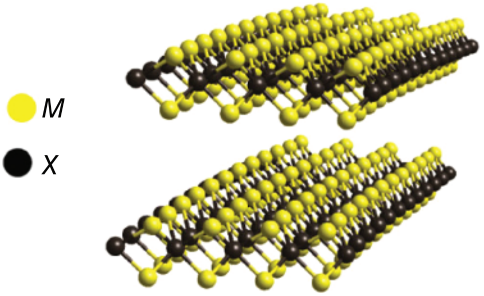

Figure 1.3 Structure of 2D molybdenum disulfide (MoS_2) layers. M atoms are in grey and X atoms are in yellow. Source: Reproduced with permission from Jariwala et al. [3].

Among various TMDs, MoS_2 is a semiconductor with an indirect bandgap of 1.3 eV. The MoS_2 will be converted into a direct bandgap with an energy of 1.8–1.9 eV when it is reduced to a monolayer, which is proved by photoluminescence (PL) measurements. Modified MoS_2 has demonstrated the ability to maintain permanent valley polarization, which is promising for valleytronics. Monolayer MoS_2 is also a candidate for spintronics due to its strong spin-orbit splitting. Monolayer TMDs have been applied in high-efficiency 2D optoelectronics devices such as light-emitting diodes (LEDs) and lasers.

1.1.2.3 2D Heterostructures

Within the wide range of materials available, the ways in which they can be combined are virtually limitless, each with its own unique properties and phenomena. For example, a tunneling device demonstration uses a thin layer of insulating hBN as a tunnel barrier between graphene sheets. 2D quantum wells can be formed by sequentially stacking different semiconducting transition metal dichalcogenides. Graphene/hBN heterostructure has been used to fabricate tunable LEDs. The development of nanoscale metamaterials has been achieved by coupling 2D materials with repeating nanostructures, revealing interesting plasmonic properties. The demonstrated applications of 2D heterostructures are in the fields of light detection, light generation, electronics, and some emerging directions such as single-photon emitters, quantum dot qubits, superconducting qubits, and topological quantum computing components.

1.2 Challenges and Prospect of Nano-optoelectronic Devices

Miniaturization of optoelectronic devices to the nanoscale offers enormous performance gains. As the volume of photoactive materials decreases, optoelectronic performance increases, including the operating speed, signal-to-noise ratio, and internal quantum efficiency. Over the past decades, the volume of photoactive materials in optoelectronic devices has been reduced by orders of magnitude. Relentless efforts have been made to overcome the limitations of further miniaturization. Among them, replacing Si with a new class of nanomaterials, such as 2D materials or heterostructures, is a promising candidate method. However, due to the lack of scalable fabrication methods, this direction is mostly limited to proof-of-concept research. Efforts are made toward the scalable fabrication of 2D heterostructures. CVD and metal organic chemical vapor deposition (MOCVD) are promising candidate methods. Nonetheless, the growth kinetics has not been fully understood. Large-scale and high-quality 2D HS with high controllability is also needed. Besides, the environmental stability of the device is a great challenge. To enable further development of nanodevices, new concepts regarding emerging materials and device configuration design need to be employed. Accordingly, the book will cover topics including (i) nanomaterials-based photodetector arrays for imaging, (ii) plasmonic photodetectors for sub-wavelength photodetection, (iii) optical resistance switch for optical sensing, (iv) optical interferometric sensing, (v) novel materials for clinical applications, (vi) computational imaging/sensing based on nanomaterials, and (vii) nanomaterial advances and on-chip integration.

1.2.1 III–V Compounds

Si is the most widely used semiconductor material due to its rich reserves, mature technology, and low cost, but it has an indirect band gap. Compared with Si, III–V compound semiconductors (such as GaAs, InP, GaN, and GaSb) and their alloys have direct band gaps. That is to say, the top of the valence band and the bottom of the conduction band are located at the same position in the wave vector space, and the electron–hole recombination does not need to exchange momentum, so it has high internal quantum efficiency and is predominantly used in optoelectronic devices [4].

GaAs is a typical III–V compound semiconductor material and is widely used in many optoelectronic fields, such as remote control, mobile phones, and lighting. Its band gap width is 1.42 eV (300 K), which can just absorb the high-energy part of the solar spectrum. Therefore, it is an ideal material for preparing solar cells. Researchers from the US Department of Energy's National Renewable Energy Laboratory (NREL) have developed a six-junction III–V solar cell with a 47.1% conversion efficiency rate under 143 suns of concentration. Its quaternary systems InGaAsP and InGaAlAs just cover the O band (1260—1360 nm, 1310 nm in the center) or C + L band (C band: 1530—1565 nm, 1550 nm in the center; L band: 1565—1625 nm) commonly used in optical communication. $In_xGa_{1-x}As$ photodetector can be used from 400 to 3600 nm, which is suitable for a wide range of applications, including optical communication, analysis, and measurement. Flexible InGaAs thin film materials have great potential in optoelectronic field. For practical fiber quantum key distribution (QKD), InGaAs/InP avalanche photodiodes are the NIR light detector of choice because they are compact and low cost, and allow cryogenic-free or even room-temperature operation [5].

Direct epitaxy on silicon is the most direct method to produce III–V compound semiconductors. However, the lattice mismatch between silicon and III–V compounds is very large (the mismatch between silicon and GaAs and InP is 4% and 8%, respectively), and this causes strain in the materials. In addition, silicon is a nonpolar crystal, whereas III–V compounds are polar. When the two are combined, an antiphase domain will exist at the interface. Therefore, obtaining high-quality epitaxial layers of III–V materials directly determines the performance of semiconductor optoelectronic devices. To solve these problems, buffer layers are usually introduced to reduce the defect density caused by the growth of III–V semiconductors on silicon. For example, the mismatch between Ge and GaAs is 0.08%, and the thermal expansion coefficient is relatively close. In order to suppress the antiphase domain, a silicon substrate with a certain deflection angle can be used, and the substrate can be pretreated at high temperature in the gas of V group elements. By this method, the diatomic steps can be formed on the silicon substrate and the surface reconstruction can be realized, which can suppress the antiphase domain.

1.2.2 Perovskites

Perovskite is a crystal material with the general molecular formula ABX3, which is octahedral in shape and has excellent structural properties. Perovskites have been intensively studied in many fields and applications owing to their excellent photoelectric efficiency and PL [6]. Especially as a promising photoelectric material, they have a wide range of applications in perovskite photovoltaic (PV) cells, LEDs [7, 8], low-threshold lasers [9, 10], electroluminescent devices [11–13], photodetectors [14], and photocatalysts [15]. Perovskite structure has strong designability and excellent photovoltaic performance, which has been a hot research direction in photovoltaics in recent years. Due to their high PL quantum efficiency, perovskites were reported as potential luminescence probes for cell imaging after overcoming the challenge of hypertoxicity by external encapsulation. Perovskite structure material is an important development path for next-generation LEDs for lighting or display. Perovskite is also the representative of the third-generation high-efficiency thin-film battery. In particular, organic perovskite is considered as a promising optoelectronic photoelectric semiconductor material. The explorations in photoelectric devices and bioscience broaden the application of perovskite. However, due to the difficulty in repetitively preparing high-quality perovskite thin films, low coupling efficiency of optical output, lead pollution, and other problems, there is still a certain distance from commercial application.

1.2.3 Organic Optoelectronic Materials

Organic optoelectronic materials are usually organic molecules rich in carbon atoms with large π-conjugated systems, which can be divided into four categories: conjugated conducting polymers, organic conjugated small molecules, phosphorescent heavy metal complexes, and aggregation-induced enhanced luminescence materials. Compared with inorganic optoelectronic materials, organic optoelectronic materials have lower costs, are thin in thickness, are light in material, and usually with higher light absorption coefficient. The material manufacturing process is simple and can be prepared in large areas and on flexible devices by solution method. In addition, organic materials have diversified structure compositions and wide property manipulation, which can obtain the required performance through molecular design. We can prepare nanodevices and molecular devices through bottom-up device assembly methods such as self-assembly. Organic optoelectronic materials are mainly used in organic solar cells, organic LEDs (OLEDs), and other display screens. Organic light-emitting materials are the key core materials of OLED panels, which directly determine the luminous characteristics of panels and are also one of the areas with the highest technical barriers. The application of organic optoelectronic materials in biomedicine has developed from early biosensors and detection to biological imaging and tumor treatment in recent years, especially high-resolution photoacoustic imaging and NIR imaging, providing a new method for the diagnosis of brain tumors and vascular tumors. Organic photovoltaics (OPV) will become an excellent candidate for energy supply on the Internet of Things (IoT) and intelligent wearable devices because of its unique mechanical flexibility, printability, and adjustable light absorption. However, organic photoelectric materials also have many disadvantages, such as low photoelectric conversion efficiency, short life, low mobility of carriers, high resistance, and poor durability. In addition, the synthesis steps of organic optoelectronic materials are cumbersome and not suitable for large-scale production. In organic semiconductors, the diffusion length of excitons is generally short, ranging between 10 and 20 nm [16]. This reduces efficiency, since the electrons accumulated as a result of solar energy conversion cannot easily flow through the photovoltaic semiconductor. Many of the advantages of organic solar cells are overridden by their relatively low efficiency, since this is the most important factor with respect to electricity generation by the cell.

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