Review article

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Optical, photonic and optoelectronic properties of graphene, h-BN and their hybrid materials

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Abstract: Because of the linear dispersion relation and the unique structure of graphene's Dirac electrons, which can be tuned the ultra-wide band, this enables more applications in photonics, electronics and plasma optics. As a substrate, hexagonal boron nitride (h-BN) has an atomic level flat surface without dangling bonds, a weak doping effect and a response in the far ultraviolet area. So the graphene/h-BN heterostructure is very attractive due to its unique optical electronics characteristics. Graphene and h-BN which are stacked in different ways could open the band gap of graphene, and form a

moiré pattern for graphene on h-BN and the superlattice in the Brillouin zone, which makes it possible to build photoelectric devices.

Keywords: grapheme; graphene/h-BN; optics; optoelectronics; phonon-polaritons; plasmons.

1 Introduction to graphene

Graphene was the first two-dimensional (2-D) atomic crystal prepared by scientists [1–4], which constitutes the basic unit of other carbon materials (Figure 1) [5]. In recent years, research on graphene has made many breakthroughs. Also, the preparation of large amounts of graphene has made a significant progress. This carbon material with an atomic thickness has excellent mechanical properties, electrical conductivity, optical properties, thermal conductivity and impermeability, which makes it attractive for many applications [6–12].

1.1 Graphene's structure and electronic band

Ideal graphene is a single layer of 2D atomic crystal with an orthohexagonal lattice structure [13]. The length of the C-C bond is approximately 0.142 nm, and the thickness of the layer is 0.35 nm.

The bonding between electrons and electrons in the graphene consists of an σ bond of the sp^2 structure and a π bond vertical to the same plane. The adjacent π bonds couple with each other to form the basis of graphene conduction [14]. Figure 2A shows the positional distribution of the A and B atoms in a single graphene cell and the energy-momentum relationship of electrons and thus behave as massless Dirac fermions [4, 16, 17]. There are A and B sub-lattices in each single cell of graphene, and the spins of the electrons on the A and B sub-lattices have chiral features with each other. Graphene is a semiconductor, which has zero band-gap, and at six points of high symmetry in the Brillouin zone (Figure 2B), the conduction

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Figure 1: Graphene: the basic unit that makes up some carbon materials such as graphite, carbon nanotubes, and fullerenes [5].

band and the valence band intersect at one point, which is called the Dirac point (Figure 2C and D) [13, 15]. Near the Dirac point, the energy and the momentum show a linear dispersion relationship $E_{2D} = \hbar v_F \sqrt{k_x^2 + k_y^2}$ [14, 15], where $v_F = 10^6$ m/s, and the linear dispersion relationship makes

the effective mass of electrons in graphene equal zero – that is, the electron in graphene is a type of massless Dirac Fermion [14, 15].

1.2 Electronic properties of graphene, which impact on optical properties

The unique crystal structure and electronic structure enable the material to have a lot of new and unique properties.

At room temperature, graphene is able to exhibit the quantum Hall effect, so it appears as an anomalous quantum Hall effect at low temperatures (below 4 K) [18, 19]. At room temperature, this behavior has been interpreted as “electrons in relativistic quantum mechanics in graphene with no quiescent mass”.

The conduction band and the valence band of graphene are symmetrical, and there are two charge carriers: electrons and holes. At the same time, as has been confirmed by experimental results the mobility of electrons and holes in graphene is the same [20], which is called the ambipolar electric field effect.

The carrier density near the Dirac point is zero, but graphene shows the existence of minimum conductivity,

Figure 2: (A) The structure of graphene lattice [14]. (B) The Brillouin zone of a graphene unit [14]. (C) The band structure of a single graphene layer along $M\Gamma K M$ [13]. (D) The band structure (top) and Brillouin zone (bottom) of graphene [15].

in the order of $4e^2/h$, between 10 K and 100 K, and the mobility is almost independent of temperature [18, 21, 22], because of Berry's phase [4]. Electrons in graphene have the characteristics of Klein tunneling, and electrons pass through the barrier with the probability of 100% [14]. In this phenomenon, the properties of massless particles are not rebounded or scattered by the presence of a barrier during the motion.

At room temperature, the speed of conduction of electrons is faster than any known conductor, and when graphene electrons move in an orbit, scattering will not occur due to lattice defects or external electrons. Therefore, the average free path of the electrons in the graphene can reach 1 μm [23], while the average material in the electronic free path in the nanometer scale. People often call it ballistic transport.

As a zero band-gap semiconductor, the unique carrier characteristics and excellent electrical properties of graphene give graphene very unique optical properties, because the optical properties of the matter are related to the electrons' state density, which directly affects all the properties of matter optics [4, 16, 17].

Ideal graphene is only a single atomic thickness, giving it optical visibility [24, 25], and transmittance (T) can be indicated according to the parameters of the fine structure [26]. Dirac electrons' linear dispersion make applications of graphene in broadband implements possible; as a result of the Pauli blocking [27, 28] we can observe its saturation absorption; the unbalanced carrier leads to hot luminescence [29, 30], and the graphene's chemical and physical properties cause luminescence [31–34], making it the ideal material for optoelectronic materials and optoelectronics.

1.3 Optical properties of graphene

1.3.1 Linear optical absorption

Graphene absorbs 2.3% of the incident light, even at only one atomic thickness, and the frequency of the incident light has nothing to do with the absorption intensity (Figure 3) [26]. These unique optical properties are generated by the electrons' conical band and holes at the Dirac point.

Graphene on top of a Si/SiO₂ substrate can be identified by using optical image contrast [24]. Geim and co-workers studied the image where SiO₂ was used as a substrate representing the relationship between multilayer graphene interference [26]. They converted the incident light and the substrate's thickness to maximize the contrast. According to the Fresnel equation [35], the photoconductivity of the suspended monolayer graphene $G_0 = e^2/4\hbar$ gives the transmissivity $T_{\text{opt}} = (1 + 2\pi G/c)^{-2} \approx 1 - \pi\alpha \approx 0.977$. This is because the valence band and the conduction band of graphene intersect near the Dirac point and the photoconductivity of graphene in the photonic band-gap over a wide $G_1(\omega) = e^2$ is independent of the frequency, but depends on the fine structure constant α , which is unrelated to the frequency. In the visible light region, the reflectance of each layer $A = 1 - T \approx \pi\alpha \approx 2.3\%$ as is shown in Figure 3A. At the atomic scale, graphene exhibits a strong broadband absorption (wavelength range of 300–2500 nm), which is about 50 times that of GaAs with the same thickness.

Electrons in graphene, as nonmass 2D particles, result in a very important nonwavenumber absorption ($\pi\alpha \approx 2.3\%$) for normal incident light below 3 eV [35]. In addition, when

Figure 3: (A) Schematic diagram of optical micrograph for different layers [24]. (B) Transmittance spectrum of single layer graphene [26].

the light energy is less than twice the Fermi level, the monolayer and multilayer graphene become completely transparent due to the Pauli barrier effect. These properties are mainly attributed to the density of graphene in electron transport of the van der Hove singular point and the electron transition between the bands, which are suitable for use in many controllable photonic devices.

1.3.2 Photoluminescence

Graphene has special characteristics and potential applications in photoluminescence and electromagnetic transport, which have created a wide range of research interests [32, 36–46]. Graphene fragments and graphene quantum dots (GQD) show unique photoluminescence properties in the preparation process; the physical and chemical treatment of graphene to reduce the coherence between π electrons is another way to make graphene photoluminescent. After a slight oxidation plasma treatment, a single graphene sheet can have bright light [31], and at this time photoluminescence has a large uniform area (Figure 4A). Likewise, bulk graphene and dispersions also exhibit extensive photoluminescence [32, 48, 49]. Etching the top layer, and keeping the lower layer intact makes preparation of the mixture possible. Based on graphene materials' photoluminescence being routinely prepared, the combination of this conductive layer and photoluminescence can be applied to sandwich-type light-emitting diodes (LEDs), with a wavelength range from infrared to blue spectral [31, 49].

A graphene quantum dot that can emit blue light by hydrothermal method has been prepared [40]. Li et al. [41] prepared green-emitting quantum dots by the electrochemical method, which can be made as the electron acceptor material for photovoltaic devices. Sun et al. used photoluminescence of oxidized graphene to image

living cells in the near-infrared region [33]; Wang et al. studied the photoluminescence mechanism of GQD [50], which revealed the excited state transfer between electrons and holes and the influence of edge effect light luminescence (Figure 4B), made in visible photoluminescence devices within the scope of the preparation of a theoretical basis.

As the size of the quantum dots decreases, graphene exhibits quantum confinement effects and unique edge effects [36, 47, 50, 51]. Some teams interpret the photoluminescence of graphene oxide as radiative recombination of e-h pairs of localization states of the sp^2 cluster [32]. The energy gap between the π^* and π states is defined by the size or the conjugate length of the sp^2 cluster [52, 53], which is more likely to be explained by the graphene edge effect and the defects associated with oxidation. Some researchers have explained that the photoluminescence of GQD is derived from radiative recombination of electrons in the free zigzag sites of the graphene edges [35], rather than the general transitions between π^* and π . No matter which luminescence mechanism is used, the photoluminescence spectra of GQD have the same characteristics; the wavelength of the emission spectrum changes with the excitation wavelength.

Therefore, the fluorescent organic has a significant impact on the development of cheap optoelectronic devices [54]. On the other hand, their toxicity and potential environmental hazards are also limited to *in vivo* applications and other applications [55, 56].

1.3.3 Saturated absorption

The excitation of the ultra-fast optical pulse causes a nonequilibrium carrier cluster between the conduction and the valence band (Figure 5) [28]. In the time-resolved

Figure 4: (A) Photoluminescence and elastic scattering image [31]. (B) Comparison of optical absorption of graphene quantum dots with NH_2 -modified GQD [47].

experiments [57], two relaxation time scales can be observed: one is the fast relaxation corresponding to the mutual collision and phonon scattering between the electrons between the conduction and the valence band, which is about 100 fs, and the other is the slower relaxation corresponding to the electron band relaxation and thermophonon cooling [58, 59].

On the picosecond scale, the linear dispersion relation of Dirac indicates that there is always resonance between electrons and holes for any excitation. The electrons and holes are solved quantitatively using the kinetic equation and the distribution function of holes $[f_e(\vec{p})$ and $f_h(\vec{p})]$, where $\vec{p}$ is the momentum of the Dirac point [28]. When the pulse time is greater than the relaxation time, the electrons reach a quiescent state during the pulse time. At the effective temperature, the electron and the hole reach the thermal equilibrium by collision. On the other hand, the number of electrons and holes determines their density of states and the total energy density [28]. Due to Paul blocking, by the factor $1 + \Delta\alpha_1 / \alpha_2 = [1 - f_e(\vec{p})][1 - f_h(\vec{p})]$, the decrease of photon absorption for each layer given by laser energy transfer from electrons to phonons.

Similarly, because of the Dirac points' linear dispersion relation, the collision of the paired carriers does not cause relaxation between the conduction and the valence band, which protects the total number of electrons and holes, respectively [28, 60]. When the energy of electrons and holes approaches the Dirac point, the phonon emission causes interband relaxation, and the spontaneous emission of hot electrons and hole groups also occurs [29, 30].

Theoretically, for a certain amount of material, a decoupling single layer graphene (SLG) is able to provide higher saturable absorption than others, because of the two-order dispersion of the graphene sheet and the

collision of the sub carriers, the relaxation of the band gap is produced [28].

1.3.4 Graphene plasmon

Surface plasmon polaritons (SPPs) are the collective oscillations of free electrons induced by external electromagnetic fields (such as photons or electrons), and have surface electromagnetic field propagation properties: the electric field intensity has the maximum value at the interface between the metal and the medium. When the vertical distance from the metal surface increases, the field strength exponentially decreases [61]. Recently graphene has been confirmed to be a plasma-derived waveguide material in the infrared frequency range [62], also known as terahertz metamaterials. Graphene has similar properties to metals in conductivity and can transport SPPs. As it has only a thin layer of atomic level, there is little need to construct surface properties, so it is called graphene plasmon (plasmons polaritons, PPs).

The graphene plasmonic properties originate from the linear optical properties of the doped graphene materials. The response of graphene to high-frequency electromagnetic waves mainly relates to its concentration of carrier and carrier mobility. The graphene carrier concentration can generally be modulated by classical doping or chemical doping, and the carrier mobility relates to the quality of graphene and dielectric environment. As graphene is a single atomic layer material, the electronic behavior is more susceptible to the surrounding environment than the bulk material, which has a larger specific surface area (Figure 6) [63–67].

The chemical potential μ and the Fermi level E_F determine the performance of graphene. By adjusting chemical doping or photoelectric reflection, the transition from electrolyte to metal can be achieved. The chemical potential μ between the conduction and the valence band gap and the in-band conductivity and graphene are relevant to the frequency ω of the incident light. When the chemical potential is $\mu < \hbar\omega/2$, the band gap transition plays a dominant role and controls the dynamic high-frequency conductivity; when the chemical potential is $\mu > \hbar\omega/2$, the transition in the band plays a dominant role and controls the megahertz range of conductivity. Under these conditions, the momentum of PPs is enhanced, so PPs can propagate in graphene. The competitive relationship between the transition of light in the band and the transition of the band gap makes it possible to couple the tunable optical response and the polarization selective coupling.

Figure 5: (A) Schematic diagram of optical excitation in graphene. (B) Low band relaxation [28].

Figure 6: (A) Schematic diagram of graphene plasma excitation. (B) Schematic diagram and test results of plasma resonance test of graphene. (C, D) Test patterns of different widths and layers [63].

1.4 Application of photonics and optoelectronics

1.4.1 Flexible electronic devices

Electronic products widely use conductive coatings, such as touch screens [68], electronic paper, organic photovoltaic cells [69] and organic LEDs [70], hence the need for low surface resistance and high transmittance of special applications. Figure 7 in comparison to the transparent conductive layer based on graphene is different from other properties of photoelectric materials, and shows their photoelectric properties [71, 72].

Graphene meets the needs of electronic and optical equipment, single-layer transmittance of up to 97.7%, but in the past people thought that performance of indium tin oxide (ITO) would be better [73]. However, considering the annual increase in the quality of graphene, the price of ITO will increase, and the cost of the deposition method preparation of ITO will increase as well. So, graphene will certainly get a larger market share. The excellent flexibility and corrosion resistance of graphene are the most important properties of flexible electronic materials equipment, but ITO cannot achieve in this respect for its lack of flexibility and corrosion resistance.

The electrical properties required for different applications of the different motors are not the same (such as surface

resistance). Due to the different production methods, there will be a variety of conductive coatings. Therefore, the electrodes of the contact screen (products requiring the chemical vapor deposition (CVD) method) have a relatively high surface conductance based on 90% light transmittance [71]. Graphene electrodes used in contact panels have the advantage of graphene having greater stability. In addition, graphene has a 10-fold higher fracture strain than ITO, which means that graphene can be used in collapsible and bendable equipment.

Flexible electronic paper is very attractive. Its bending radius is in the range of 5–10 mm. This requirement is very easy to achieve for graphene. And graphene can absorb visible light, which for the color of electronic paper is very important. However, the graphene electrode contact resistance and metal loop are still a big problem.

Despite the relatively high resistance of graphene films, the advantages of the flexibility and high mechanical strength of graphene ensure that the graphene equipment can have more flexible applications.

1.4.2 Photodetector

One of the most widely researched optoelectronic devices, graphene photodetectors, are and can be used in the wide-band spectral region between ultraviolet and infrared. The ultra-wide working bandwidth is an advantage of the graphene photodetector, allowing them to be used in high-speed data communications. The high carrier activity of graphene provides a carrier for rapid extraction of the picture, as it allows for higher bandwidth operation. At the reported velocity of saturated carriers, the bandwidth of the graphene photodetector due to time constraints is expected to reach 1.5 THz [88, 89]. In fact, the graphene photodetector has the maximum bandwidth of 640 GHz due to the delay of the capacitor rather than the delay of the transfer time [88].

At present, the graphene photodetector uses a local potential change near the surface of the metal-graphene to extract the photodetector carrier [90, 91]. The optical response rate can reach 40 GHz; the detector-operating rate can reach 10 GHz. However, the maximum response rate is relatively low due to the limitation of the smaller effective detection area and the thin graphene to the absorption rate.

There are many solutions for increasing the graphene photodetector sensitivity, for example, using nanostructured plasma to enhance the local optical electric field or to increase the photo-graphene interaction length by combining with a waveguide [92, 93].

Without the band gap of graphene, low response and low optical gain and limits the applications of graphene

Figure 7: Graphene as transparent conductor. (A) Transmittance for different transparent conductors: GTCFs [71], single-walled carbon nanotubes (SWNTs) [72], ITO [73], ZnO/Ag/ZnO, and TiO₂/Ag/TiO₂ [74, 75]. (B) Thickness dependence of the sheet resistance. The blue rhombuses show roll-to-roll GTCFs based on CVD-grown graphene [71]; red squares, ITO [73]; gray dots, metal nanowires [73]; green rhombuses, SWNTs [72]. Two limiting lines for GTCFs are also plotted (enclosing the shaded area). (C) Transmittance versus sheet resistance for different transparent conductors: blue rhombuses, roll-to-roll GTCFs based on CVD-grown graphene [71]; red line, ITO [73]; grey dots, metal nanowires [73]; green triangles, SWNTs [72]. Shaded area enclosed by limiting lines for GTCFs calculated using n and μ as in (B). (D) Transmittance versus sheet resistance for GTCFs grouped according to the production strategies: triangles, CVD [10, 71, 76, 77]; blue rhombuses, micromechanical cleavage (MC) [78]; red rhombuses, organic synthesis from polyaromatic hydrocarbons (PAHs) [79]; dots, liquid-phase exfoliation (LPE) of pristine graphene [78, 80–82]; and stars, reduced graphene oxide (RGO) [83–87].

based photoelectric detector, even the superfast and broadband optical response of graphene. Figure 8 shows a photodetector based on graphene-Bi₂Te₃ heterostructure which overcomes these difficulties [94]. Owing to the topological

Figure 8: Photodetector based on graphene-Bi₂Te₃ heterostructure [94].

insulators family with a small hexagonal symmetry structure similar to that of graphene with zero gap materials, the photocurrent device can be effectively enhanced and fails to detect a decline in the spectral width. The result shows that the graphene Bi₂Te₃ photodetector has a higher optical response and a higher sensitivity than the pure monolayer graphene apparatus, and the detection wavelength range of the device is extended to the near infrared region (980 nm), and the communication band (1550 nm).

1.4.3 Optical modulator

An excellent optical modulator is able to achieve the performance through stripping the resulting graphene, which absorbs a small amount of incident light from a broad spectrum of light and is able to respond quickly. In order to achieve these properties, in a single graphene layer [95], the inter-band transition photoelectrons are modulated by

a driving voltage across a wide band to obtain an optical modulator with a bandwidth in the near-infrared region of more than 1 GHz [96]. The use of mutually constrained double graphene can reduce the delay in the RC delay by providing some structural change, providing an area that can reach hundreds of gigabits. Theoretically, operating light modulators with bandwidth in excess of 50 GHz cannot be achieved [93]. Graphene is a latent material for megahertz wireless communications because the loss of light in graphene is much less than in precious metals.

Liu et al. assembled and fabricated an electroabsorption modulator based on graphene waveguide integration for the first time [96], in which actively tuning the Fermi level of a monolayer graphene sheet achieves modulation (Figure 9). The gigahertz graphene modulator demonstrates a strong electroabsorption modulation of 0.1 dB μm^{-1} and operates over a broad range of wavelength, with a range of 1.35–1.6 μm .

1.4.4 Mode-locked laser/THz generator

Ultrafast passive mode-locked lasers have been used in spectroscopy, micro-materials processing [97], biomedical [98] and safety applications. They are often used as a saturable absorber, by selecting high-intensity light transmission to cause the modulation of light intensity. Compared to the semiconductor saturable absorber [99], graphene monolayer absorbance is very high, which in the low light intensity of the wide band area can be saturated [28, 100].

Figure 9: Schematic diagram of graphene optical modulator [96].

Controllable modulation depth, high thermal conductivity, wide frequency tuning, relaxation time and high damage threshold of the ultrafast carrier are all the advantages of the graphene saturated absorber [26, 101, 102].

Scientists have devoted much of their research to fiber and solid-state lasers [103]. However, people can also use graphene-saturated absorbers in semiconductor laser technology. Wavelength multiplexing eliminates the need for optical interconnections with a series of lasers of different wavelengths. Using a single laser in different longitudinal modes can generate different wavelengths such as mode-locked lasers [104]. Active mode-locked silicon hybrid lasers have been studied to meet the needs of laser technology [105], but graphene-saturated absorbers can provide simple passive mode-locked semiconductor lasers for operation and processing.

Wan et al. [106] prepared high-quality graphene using the CVD method on copper. It was the first time the use of high-quality single-graphene as a saturable absorber (SA) was used to prepare the stability of the diode-pumped passive mode-locked Tm: YAP laser (Figure 10). The absorption pump power is 7.67 W, and the output power of the laser can reach 256 mW at 1988.5 nm, which is the center wavelength. When the pulse frequency is 62.38 MHz, the pulse energy can reach 4.1 nJ [106]. Studies show that using graphene to create low-cost and ultrafast laser is promising.

2 Introduction of h-BN

Hexagonal boron nitride (h-BN) is the only phase structure in all phases of boron nitride [107–110], which is hexagonal, white and similar to the layer structural features of graphene, also known as “white graphene”. Each atomic layer is composed of B and N atoms alternately arranged in an infinite extension of the hexagonal grid (Figure 11), the atomic layer along the C axis direction in accordance with the ABAB

Figure 10: (A) Assembly diagram of mode-locked laser based on graphene. (B) Test pattern of graphene mode-locked laser [106].

Figure 11: (A) The planar structure of 2D h-BN [110]. (B) SEM surface photographs of the h-BN film [111].

order. In each layer, B and N atoms are strongly bonded by the sp^2 covalent bond, with a bond length $a=b=0.2504$ nm. The layers are connected by a weak Van der Waals force. The bond length is $c=0.6661$ nm and density is 2.28 g/cm³. Therefore, h-BN along the C axis direction of the bonding force is very small; the space of atomic layer is large; it is easy to slide between layers; and it is a good lubricant. Hexagonal boron nitride has a wide range of applications due to its excellent physicochemical properties [111–118]. It can be used as an oxidizing additive for refractory materials, insulating films in electronic devices, transparent insulators for electroluminescent devices due to its transparent in X-ray and visible regions, and in the manufacture of sub-nanometer VLSIs protective film and so on.

2.1 Electronic band structure of 2D h-BN

Graphene and 2D h-BN have a similar honeycomb structure. In 2D h-BN, each cell contains a B and an N atom, with a total of eight electrons; sp^2 hybridization is performed between B

atoms and N atoms; each B (N) atoms and the most immediate of the three N (B) atoms generate three σ bonds; there are six electrons filled into the σ orbit; the remaining two electrons in the $2p_z$ state forms the vertical plane π bond [119].

The single layer (2D) h-BN is directly band-gap, top of valence band and bottom of conduction band are all at the high symmetry point K. Homeostatic model assessment (HOMO) and LUMO of the system are determined by the π and π^* that state on the N atom and the B atom, respectively. The bonding combination of B- sp^2 and N- sp^2 orbitals forms the bond between the nearest B atoms and N atoms. Electron transfers from B atom to N atom, because of the electronegativity difference between B atom and N atom. Between B and N, the bond shows ionic properties, opposite to the pure covalent bonds in graphene. The properties of h-BN are mainly due to the charge transfer between nitrogen and boron atoms. Because of this, the complementary structure and honeycomb structure of graphene arises with h-BN [112, 113].

Figure 12A shows the structure and charge of atomic charge transfer between nitrogen and boron atoms, and

Figure 12: (A) Optimized atomic structure, energy bands of 2D h-BN. (B) Density of state of 2D h-BN [119].

Figure 12B shows density of states of the 2D h-BN electronic structure. High density around N atoms is represented by contour plots of total charge. The charge density of 2D h-BN minus charge densities of free B and N atoms equals the difference in charge density, i.e. $\Delta\rho = \rho_{\text{BN}} - \rho_{\text{B}} - \rho_{\text{N}}$. The charge transfer from B to N atoms can be indicated by high-density contour plots around N atoms protruding toward the B-N bonds [114]. 2D h-BN is a semiconductor. The calculations of electronic energy bands and h-BN crystal are similar [115]. As bonding and anti-bonding combinations of $\text{N-}p_z$ and $\text{B-}p_z$ orbitals, the π and π^* bands of graphene crossing at the K and K' points of the BZ open a gap in the 2D h-BN. $\text{N-}p_z$ makes a significant contribution for the filled band at the edge of the valence band. The calculation of band gap is not direct, $E_g = 4.64$ eV. TDOS and partial density of states are similar to those of the h-BN layered crystal as shown in Figure 12.

2.2 Optical properties of h-BN

Boron nitride is the lightest, strongest ionicity group III–V material, whose optical properties have drawn people's attention. In the short-wave LEDs, semiconductor lasers, and photodetectors, boron nitride has a wide range of applications. Especially, in recent years, h-BN emission spectra have been found to have very strong excitonic emission peaks in the ultraviolet region [116, 118, 120], which can be applied to deep ultraviolet lasers. The optical properties of boron nitride nanostructures also draw great interest [121–125].

2.2.1 Infrared characteristics of h-BN

As is known, Fourier transform infrared (FTIR) spectroscopy, which has been used to examine newly prepared products, is the effective method to characteristically determine the structure of new experimental products, so some researchers used FTIR to research the structural nature of h-BN [126–129].

Some researchers obtained data on BN vibrations in h-BN, where h-BN is in the state of a single crystal. The peak value is 1365 cm^{-1} [127]. The phonon modes of turbostratic h-BN are 792 and 1384 cm^{-1} . From some of the reports, we know that the phonon modes have shifted to 800 and 1372 cm^{-1} when h-BN is in a multilayer state. On the other hand, the phonon modes of h-BN tubes shift to 811 and 1377 cm^{-1} , when h-BN is in the polycrystalline state [128]. From Figure 13, we can see that there are two peaks at 1374 and 818 cm^{-1} from the FTIR spectrum, which is due to the strong vibrations of BN in the h-BN

Figure 13: Infrared spectra of h-BN [126].

nanosheets. With the aid of FTIR, the structural properties and phase composition of experimental h-BN products were revealed. We also know that the peak is at 1374 cm^{-1} , which belongs to the transverse optical modes of the sp^2 bonded h-BN when B-N is in the plane. When nitrogen-boron-nitrogen is out of plane, a peak appears at 818 cm^{-1} , which could belong to the bending vibration of B-N-B [126, 129]. However, there are no absorption peaks belonging to the raw materials or any impurities that have emerged in the visible region.

2.2.2 UV characteristics of h-BN

With deeper research, the theoretical calculation and experimental verification have shown the ultraviolet absorption spectrum of the 2D h-BN materials [110, 111, 130, 131].

By the simulation of the idea on 2D h-BN nanomaterials, Wang et al. calculated the single layer h-BN's absorption spectrum by using DFT and DT-DFT methods, and the spectrum of the 2D single layer h-BN materials revealed the optical absorption property of h-BN [110]. From Figure 14A, we can see three strong absorption peaks in the spectrum. On the other hand, there is a shoulder around 210 nm , which in the deep UV region. The three absorption peaks are around at 197 , 203 , and 208 nm , respectively. By using the charge different density method, the absorption peaks are due to strong charge transfer and the vibration of the BN.

The theoretical calculation is consistent with the experimental verification. Jin et al. got the deep UV absorption spectrum of the h-BN experiment materials. There is a strong absorption peak at 234.8 nm , and

Figure 14: UV-vis optical absorption spectra of 2D h-BN nanometer material. (A) Simulation model [110]. (B) Experimental h-BN nanosheets at 293K [111].

the optical energy band gap corresponds to 5.28 eV (Figure 14B) [111]. Their data are basically the same as the previous researchers, just as 5.2 and 5.14 eV, which were made by Hoffman et al. and Stenzel et al. [130, 131], respectively. On the other hand, an absorption peak around 263.1 nm appeared in the optical absorption spectrum, which corresponds to the optical energy band gap with the value of 4.71 eV. They made sure that the defect level of the boron nitride nanosheets resulted in this absorption peak, and the absorption peak energy corresponds to the difference between 5.28 (corresponding to the optical energy band gap) and 0.63 eV (corresponding to the activation energy of the donor level). By using the TSC method, the observed result can prove the influence of the donor level, which leads to the emergence of the absorption peak at 263 nm.

Both the results of the experiment and simulation have proved once again that 2D h-BN has a strong optical response in the deep UV area.

2.2.3 Luminescence property of h-BN

As one of the semiconductor materials, the bandgap energy properties and the band structure of h-BN materials have been studied for some years. With the accelerated development of research, both direct bandgap and indirect bandgap have been revealed slowly. Luminescence is one unique optical feature of h-BN [111, 116, 132–135].

2.2.3.1 Cathodoluminescence property

Watanabe et al. studied the optical properties and electrical properties of the h-BN crystal [116]. There is a

cathodoluminescence (CL) spectrum of experimental h-BN materials at room temperature shown in Figure 15A. From Figure 15A, there is a strong peak in the spectrum of the h-BN single layer crystal, which had been successfully made by them. The peak appeared at 215 nm with the bandgap of 5.76 eV at the room temperature. On the other hand, there is a shoulder structure appearing at 300 nm, which corresponds to the bandgap of 4 eV. By researching this shoulder, either the structure of h-BN defects or the impurities in h-BN might cause this result, just as in oxygen and carbon [132]. The ratio of two peaks of about 100 times are all in the deep UV region.

2.2.3.2 Photostimulated luminescence

As described earlier, CL spectroscopy had been thought to exist corresponding to near-band-gap structure, which is in the deep ultraviolet region. The photostimulated luminescence (PSL) is thought to result in the capture at the free carrier at the distal lattice point, the visible light makes the carriers recombine in these traps [120, 133, 136].

Through the research of Figure 15B [133], PSL has revealed that the state depends on the infinite lifetime, in which the depopulation is triggered with incident light. When the energy of the incident light is beyond 5.5 eV, the PSL spectrum appeared. On the other hand, the quality of the sample or defects may destroy the crystalline symmetry, which will make the hypothetical dark state accessible. There are no free exciton emissions in the figure of the case, so people considered that the strong coupling of the singlet with triplet excitons leads to the emergence of the results and a shortened lifetime. Accordingly, there is no exciton state of long

Figure 15: (A) Cathodoluminescence spectrum of h-BN [116]. (B) PSL excitation spectrum and PLE spectrum of polycrystalline h-BN [133]. (C) Phosphorescence decay curves of different photon excitation energies [133]. (D) Laser emission spectrum of h-BN [116].

lifetime in the case. In Figure 15B, using open circles, a small part of the PSL excitation spectrum is represented corresponding to the whole spectrum, and the whole measured spectrum is shown as an inset in Figure 15B. The range of energy from 5 to 7 eV is considered as the PSL excitation energy. The spectrum to be indexed increased, then it reached the maximum at 5.7 eV. After this, the growth of the image became slower until it reached the next maximum at 6.10 eV. After a brief drop, the image adds progressively and reaches the final at 7 eV. The purple line represents the PLE spectrum, which is the near band-edge luminescence with the value of 5.3 eV.

As we know, we cannot measure the band-gap energy by using the PSL excitation. But we can get valuable information of exciton or the band-edge energy position by the combination of the PLE spectrum.

2.2.3.3 Phosphorescence property of h-BN

From Figure 15C [133], the phosphorescence decay curves of different photon excitation energies can be seen, which range from 5.4 to 5.9 eV. When the energy at $E_{\text{exc}} \leq 5.5$ eV, the phosphorescence decay curves can be characterized by monoexponential decay during the characteristic time of 5.8 s. The PM dark noise is shown in the figure by the dotted line. When the energy is $E_{\text{exc}} \geq 5.6$ eV, the long-lived part of low intensity arises, and it is the higher part of the figure is just like a plateau. The long component of the recombination at large distance tends to infinity, which belong to the charges. When the excitation energy increased from 5.1 to 5.9 eV, the intensity of the phosphorescence increased about 20 times.

Some researchers studied the phosphorescence spectrum, and they considered it as related to the forbidden dipole, that is, dark exciton states. Watanabe et al.

considered the coupling between the dark exciton states and the white exciton states [116], which makes the photoluminescence spectra arise in the absorption spectrum of h-BN monocrystals.

2.2.3.4 Laser emission

Figure 15D is the laser emission spectrum of h-BN, which was measured by Watanabe et al. [116]. When light is transmitted through the experiment, the sharp fringes of Figure 15D correspond to the fringes of the absorption spectrum, and the fringe's wavelengths vary from 213 to 224 nm at low temperature at 8 K. This fringe mode spacing can be expressed with a formula, which represented as $\lambda^2/2D(n - \lambda dn/d\lambda)$, D expresses thickness of h-BN, n means index of refraction, and λ denotes the wavelength.

The spectrum of laser emission spectrum reveals that the change of emission wavelength range begins at around 208 nm and ends at around 240 nm. The fringes rise sharply from 208 to 215 nm and achieve maximum intensity at 215 nm, where the strong UV luminescence happens with the energy at 5.76 eV. From 215 to 240 nm, the fringes sharply decline. On the other hand, when the wavelength is at 240 nm, the emission intensity is close to zero. When $dn/d\lambda$ changes, which represents the dispersion term, it can lead to the change in mode spacing. Similar to the exciton polariton effect near the exciton energy level, the exciton effect determines the abnormal dispersion.

2.2.4 Phonon polaritons on h-BN

Optical phonons coupling of the photons in polar crystals, in the collective modes are called phonon polaritons. These materials show optical phonons, which are similar to some polar Van der Waals solids, and the property might be usually called polaritonic effects. Because of the strong phonon resonances, h-BN becomes a good polaritonic effect material.

Dai et al. studied this character of h-BN by using s-SNOM [137]. They adjusted the intensity of incident light and changed the number of layers to achieve the realization of the phonon polariton. Figure 16A is the dispersion relation of phonon polaritons of h-BN. From the image we can know that AFM tip alters the range of momenta, which supports phonon polaritons of h-BN. The polariton propagates rapidly on the surface of boron nitride. With the change of the incident wavelength, the dispersion relation of the phonon polariton is expressed in

Figure 16A. Figure 16B shows the image of different layers of h-BN and different lengths of the edge whereas Figure 16C and D shows experimental measurement of polariton wavelength and the data are predicted according to the principle, which are in good agreement.

From their study, we can know that the phonon polaritons can confine and tune electromagnetic energy on the nanometer scale. By altering the layers number, the wavelength and the confinement of phonon polaritons can be designed.

2.3 Potential applications of h-BN

Boron nitride has such optical and photoelectric properties that have broad application prospects in the optical field, especially in the deep ultraviolet region.

2.3.1 MSM photodetector

The h-BN epilayers have some features, such as optical absorption and dielectric strength, and as a result, they have potential for application as deep UV detector materials.

Li et al. synthesized h-BN epilayers by using the CVD method [138]. Analogous to the optical absorption property of graphene, they tested and found the absorption coefficient as about $7 \times 10^5/\text{cm}$ of band edge in h-BN. Both the dielectric strength and the absorption coefficient are better than those of a wurtzite AlN. Figure 17 shows the typical I-V performance of MSM detectors, which is based on the h-BN epilayer. When the bias voltage is 100 V, the low dark current is 200 pA and the current density is 10^{-10} A/cm^2 , respectively. There are other data of spectral responses corresponding to the different bias voltages in the figure. From Figure 17B, there is a sharp peak of optical responsivity at 220 nm and the cut-off wavelength at 230 nm, respectively. It is in good agreement with the fluorescence emission peak of the band-edge of h-BN, which is at 227 nm (5.48 eV). On the other hand, there are no detectable responses in low frequency region up to 800 nm. However, the visible rejection ratio of h-BN MSM detectors in the UV region is two to three orders of magnitude shorter than that of the AlN detectors [139, 140].

Based on the above study, they summed up several advantages such as high deep ultraviolet to visible rejection ratio, due to the high absorption of the thin active layers; it is suitable for oxidation resistance and chemical inertness and high dielectric strength.

Figure 16: (A) Sketch map of phonon polaritons of h-BN [137]. The test spectrum line of h-BN with different layers, width in (B)–(D).

Figure 17: (A) I–V characteristics of photodetector. (B) Relative spectral response of detector [138].

2.3.2 Deep UV emitters

In the P-type conductivity demonstration progress of the epitaxial growth the h-BN method of the epitaxial layer,

which represents the p-layer revolutionary and overcomes the Al-rich AlGaN deep purple problems inherent in low p-type conductivity using a special deep UV device application. However, the epitaxial growth of h-BN on AlGaN is

a prerequisite for the formation of a P-type AlGa_N deep UV device structure [141–144].

Majety et al. used the method mentioned earlier to assemble the heterostructure, which was prepared for the p-type h-BN and AlGa_N deep UV device structure [144]. They used the CVD method to prepare h-BN and the AlGa_N/AlN/Al₂O₃ templates. The epitaxial layers of h-BN were also highly insulated in the AlN and N-type AlGa_N templates, trying to prove that h-BN/AlGa_N p-n junction is grown by Mg doping. By testing the diode performance of the heterostructure, they demonstrated the feasibility of the p-type h-BN as electron blocking of its high conduction, which can be made as a p-contact layer of deep ultraviolet emitters (Figure 18A,B). The characteristics of I–V correspond to the p-n structure, which is doped Mg in a buffer layer annealed at a temperature of 1020°C. The test values under different temperatures are shown in Figure 18B. The test results showed that these p-n heterostructures have wide application prospects in the application of high efficiency deep UV photovoltaic devices.

2.3.3 Far UV plane-emission device (LED)

Some researchers have been hoping to replace the traditional far UV lamps with the high efficiency of a solid-state device with a long service life. But, due to the low efficiency of UV lamps, research still continues for developing far UV devices with high performance [145–147].

Watanabe et al. studied the potential application of h-BN as far UV fluorescent materials [147]. The height of

the luminescence of h-BN far UV emission planar compact device is equipped with a field emission array as the excitation source, which proves that it is a stable operation and has an output power of 0.2 MW at 225 nm. Due to its low current consumption during operation, the device can be driven by a dry battery. This convenient far UV device may prove useful in chemical and biotechnological applications such as chemical modification, photo-catalysis and sterilization. The operating state of a FUV plane-emitting device consisting of a field emitter as a cathode, the power of h-BN on the screen, a vacuum chamber, and a wire electrode around the screen is shown in Figure 19A, which is driven by a dry battery. Figure 19B shows a FUV plane-emission device. The output power of the device is shown in Figure 19C, from it, we know that, with the increase of the acceleration voltage from 3 to 8 kV, the output power increases nonlinearly from 0.02 to 0.25 mW. The output spectra of this device are shown in Figure 19D. From Figure 19D, there are three spectral lines in the figure corresponding to different anode voltage, which the emission intensity increases with the increase of anode voltage. The emission wavelength ranges from 215 to 400 nm and there is a strong peak around 227 nm.

3 Introduction of graphene/h-BN Van der Waals heterostructure

Different Van der Waals heterostructures can be formed by different 2D materials with Van der Waals forces, so they can show the properties that the 2D materials do

Figure 18: (A) I–V characteristics of a p-hBN: Mg/n-Al_{0.62}Ga_{0.38}N/AlN structure. (B) I–V characteristics of emitters at different times and temperatures [144].

Figure 19: (A) Photograph of different far-ultraviolet (FUV) plane-emission device in operation. (B) Photograph of a battery-driven FUV plane-emission device in operation. (C, D) Test spectrum line of FUV [147].

not possess. As the substrate of graphene, various properties of hexagonal boron nitride are the best. They form heterostructures (Figure 20) and have become one of research hot spots [148–152]. The emergence of this artificial heterojunction provides researchers with a great deal of flexibility for the design of different structures and devices [150].

3.1 The structure of graphene/h-BN Van der Waals heterostructure

Graphene/h-BN is one of the most typical representatives [153–159]. Graphene and hexagonal boron nitride combine together; the graphene surface will appear as moiré stripes (Figure 21A); moiré fringe cycle is closely related to the

angle between those two. This moiré fringe can be regarded as a modulation of the periodic potential of graphene on a boron nitride substrate, leading to the reconstruction of graphene bands, such as the generation of self-similar superlattice sub-bands and the opening of the graphene gap. The lattice orientation of graphene is the same as that of boron nitride, and its energy is the lowest and most stable.

As an insulating material with a band gap of 5.97 eV, hexagonal boron nitride has an atomically flat surface, no dangling bonds, weak doping effect, etc. The surface roughness is extremely low, shows weak Van der Waals forces to graphite, and has minimal impact on the graphite carrier transport properties, and the mismatch degree of it and the graphite thin lattice is only 1.7%, with no doping effect to graphite. Therefore intrinsic physical properties of the graphene can be maximally maintained (Figure 21B and C).

Figure 20: Graphene/BN heterostructure and typical transport property. (A) Atomic force microscopy image shows a high coverage of monolayer graphene along with a small portion of bilayer graphene (bright area $\sim 0.3\%$) and bare BN (dark area $\sim 3\%$). The inset shows a high-resolution AFM image of the graphene/BN moiré superlattice with a period of 151 nm. (B) Optical micrograph of a two-terminal field-effect graphene/BN device on a SiO_2/Si substrate. (C) Gate-dependent resistance of a typical graphene/BN device at room temperature [148].

Figure 21: (A) Schematic of the moiré pattern for graphene (gray) on h-BN (red and blue) [149]. Graphene/h-BN heterostructure schematic diagram. (B) Top view and side view [133]. (C) Two-terminal magnetoconductance of device A1 up to 45 T [149].

More importantly, a 2D superlattice structure formed by graphene on h-BN can control the graphene band structure and form an additional Dirac point [160–163]. In order to explore a series of new physical phenomena such as the Hofstadter butterfly spectrum (Figure 21D), it provides an effective means [159]. The graphene electron mobility on the h-BN substrate can be comparable to that of free-floating graphene, and the substrate-supported graphene/hexagonal boron nitride structure is clearly more suitable for the design of graphene-based electronic devices [164, 165].

3.2 Energy band gap structure of graphene/h-BN Van der Waals heterostructure

The quantum nature of electrons generates a band structure that determines the conduction of electrons and the optical properties of the material. Long-range superlattices, on the other hand, can produce microstructures that are dispersed in a better energy scale crossing a reduced Brillouin zone, which produces

negative differential conductance and Bloch oscillation, and so on.

With the development of research, the arrival of Van der Waals heterojunction of high-quality graphene/h-BN (deviation angle of less than 1°) has significantly changed the status quo [151, 162, 166]. In this heterostructure, the periodic potential of the electrons in the graphene is exploited by the hexagonal moiré fringes generated by the inconsistency between the two crystals. The microstructures of Dirac electrons have also been demonstrated by scanning tunneling, capacitance and optical microscopy. These studies illustrate the electronic structure of the so-called Hofstadter butterfly that appears in a quantized magnetic field.

Figure 22 shows the key features of the micro-band energy dynamics in the moiré superlattice [166], and points out the direction of new transport effects to be explored further. At the technical level, a clear demonstration of such a micro-strip conductance implies that graphene/h-BN is a practical platform based on micro-band energy physical devices. The high efficiency of the photocurrent generated at the edge of the graphene superlattice in the magnetic field may be caused by the transition orbit observed by the researchers; in addition, Hz devices such as a Bloch oscillator can benefit from longer scattering times in the system.

Wang et al. reported direct experimental results on the dispersion of SDCs in 0° -aligned graphene/h-BN heterostructures by using angle-resolved photoemission spectroscopy. It reveals SDCs at the corners of the superlattice Brillouin zone, and at only one of the two superlattice valleys [167]. They also made the gaps of approximately 100 meV and approximately 160 meV, which observed at the SDCs and the original graphene Dirac cone, respectively (Figure 23). Their research result shows the important role of the potential of a strong inversion-symmetry-breaking perturbation in the physics of graphene/h-BN, and bridges the gaps of critical knowledge in the band structure engineering of Dirac fermions through a superlattice potential [168].

3.3 Optical and photoelectric properties of graphene/h-BN Van der Waals heterostructure

Some 2.3% of the incident light is absorbed by graphene, despite the fact that it has only one atomic thickness, and the absorption intensity is irrelevant to the frequency of the incident light. The absorption intensity corresponds

Figure 22: (A) Calculated miniband structure of the graphene/h-BN superlattice. (B) Representative ensembles of simulated skipping orbits emanating from an emitter (red star) at the boundary of the graphene/h-BN superlattice possessing the miniband dispersion [164].

Figure 23: Observation of gap opening at second-generation Dirac points of graphene/h-BN [167]. (A)–(C), ARPES data through the SDPs along different directions. (D)–(F), EDCs between the momenta indicated in (A)–(C). (G)–(I) Fitting results of the EDCs across the SDPs in (A)–(C) with two (G, H) or three (I) Lorentzian peaks.

linearly with the number of graphene layers. Graphene has a broadband absorption characteristic, especially in the visible region, where the response to the optical is obvious. Additionally, h-BN has an absorption peak in the ultraviolet region. In other words, the graphene/h-BN van der Waals heterostructure may have peculiar characteristics in the correlation response [169–174].

3.3.1 Optical advantages of graphene/h-BN in visible and SW-NIR regions

Wang et al. calculated the optical properties of this structure in the entire optical region and the electron transfer in the excited state by DFT and TD-DFT [133]. The results show that the graphene has a strong optical absorption peak in the visible and near UV regions, whereas the single layer hexagonal boron nitride has optical absorption in the deep UV region. When they compose heterostructures, boron nitride has little absorption effect on graphene; from the situation of SLG and heterostructures in the excited state electron-hole transfer, it can also be seen in the visible region, between graphene and boron nitride there is no charge transfer, but inside graphene itself there is charge and hole transfer (Figure 24A). The graph shown in Figure 24B also confirms that the influence of boron nitride on the graphene as a graphene substrate is negligible, which further theoretically explains that for the production of graphene-based optoelectronic devices, boron nitride is a very good substrate.

3.3.2 UV features of graphene/h-BN

Recently, Liu Zhongfan Research Group of Peking University successfully completed the preparation of patterned graphene/h-BN single crystal heterojunctions [169]. Prior to CVD growth, PMMA was coated on the copper foil surface by electron beam etching. These PMMA particles, like “seed”, act as centers of nucleation, allowing

Figure 24: (A) Charge-transfer densities for the strong electronic transitions in single-layer on single-layer h-BN substrate with top and side views, where the green and the red stand for the hole and electrons, respectively. (B) The calculated absorption spectra of SLG and graphene/h-BN [133].

patterned growth of graphene during preparation of CVD. Meanwhile, PMMA particles also controlled the nucleation density and grain size, and provided a possible direction for the high quality graphene/h-BN heterojunction growth. In the experiment, they also concluded that the optical properties of the heterostructure, UV-visible absorption spectra showed that at 270 and 200 nm there are graphene and h-BN absorption peaks; at 550 nm graphene/h-BN van der Waals heterojunction has high visible light transparency, which provides a possibility for heterojunction to be used in optoelectronic devices (Figure 25).

3.3.3 Negative refraction effect

Recently, the theoretical and experimental research on the hybridization between the graphene plasmon polariton and hexagonal boron nitride phonon polaritons have been extensively studied. In this regard, the study of the stacked structure of graphene and h-BN as the multilayer structure of the crystal is less [175–178].

As tunable materials, graphene and h-BN stack of hyperbolic crystal can be adjusted by adjusting the chemical potential of graphene to give more freedom.

Sayem et al. studied on the properties of the crystal structure stacked by graphene and h-BN [178]. There are two schematic diagrams of negative refraction in Figure 26B, h-BN and graphene/h-BN hyper-crystals, respectively. Which the hyper-crystals stacked by SLG and h-BN. By matching the wave-vector ($\theta_{rk,hc}$) and pointing vector ($\theta_{rs,hc}$), a function corresponding to the incidence angle at wavenumber 810 cm^{-1} , which corresponds to the difference from the graphene chemical potential value. The 2D map of refraction angles is shown in Figure 26C, for $\mu_c = 0.25\text{ eV}$. Figure 26D shows us the reflection for different μ_c . From 725 to 850 nm, the reflection increases slowly with the increase in wavenumber. When the wave-number increases to 800 cm^{-1} this reflex is stopped. In the range of wavenumbers from 800 to 820 cm^{-1} , the reflection decreases sharply. After 820 cm^{-1} , the reflection increases sharply, reaching a maximum value near 830 cm^{-1} , and then the reflection decreases slowly, but the small μ_c refraction but high.

The all-angle negative refraction of the hyper crystal is much higher than that of bare h-BN. On the other hand, graphene can completely control the negative refraction of the optical properties of boron nitride and the transmission characteristics of the boron nitride structure without hindering the negative refraction.

Figure 25: Electrical and optical properties of patterned G/h-BN. (A) Schematic depiction of FET devices based on G/h-BN stacks. (B) Source-drain current (I_{ds}) and channel resistance (R) as a function of back gate voltage (V_{gate}) measured at room temperature. (C) Optical image of patterned FET devices, fabricated using transferred G/h-BN patterns on 300 nm SiO₂/Si. (D) Close-view of (C) showing 3×2 devices. (E) UV-vis transmittance of G/h-BN (blue) and h-BN (red). (F) Photograph of the transparent graphene FET arrays fabricated using G/h-BN stacks on the quartz glass [169].

Figure 26: (A) Schematic representation of negative refraction in bare h-BN and GhHC. (B) Refraction angles for the pointing vector (symbols “o”) and wave-vector (solid lines) for GhHC as a function of incidence angle at wavenumber 800 cm⁻¹ for different values of the chemical potential of graphene. (C) 2D map of the refraction angles for the pointing vector as a function of wavenumber and incidence angle for $\mu_c = 0.25$ eV. (D) Reflection of h-BN and GhHC as a function of wavenumber with an incidence angle 30° [178].

3.3.4 Raman characteristics of graphene/h-BN superlattices

As a fast and nondestructive detection technique, Raman spectroscopy is widely used in the qualitative study of some materials. In particular, it is much sensitive to the alignment between graphene and h-BN [179–181].

Eckmann et al. studied the Raman spectra of the heterostructure stacked by graphene on h-BN, where the lattice of two kinds of materials is perfectly aligned [182]. Figure 27A is the schematic diagram for graphene/h-BN. Due to the difference of the length of the B-N bond and the length of the C-C bond, graphene and h-BN, which is the same as the honeycomb lattice structure of the six party, have been shown to form a superlattice after being stacked into a heterostructure. The wavelength λ_m and the low superlattice Dirac point (SPD) energy E_{SDP} corresponds

to the stacking angle θ between graphene and h-BN. The linear dependence of FWHM (2D peak) and moiré wavelength for twist angles is below 2°. They make the function $\text{FWHM (2D)} \Delta 5 + 2.6\lambda_m$. The comparing spectral lines between graphene/h-BN and tBLG (twisted bilayer graphene) of peak R' as a function of the mismatch angle are shown in Figure 27C. From it, we can know that, the position of peak R' increases with the increase of the lattice alignment angle of graphene and h-BN. The theoretical calculation of the two structures is basically the same. Figure 27D is the Raman spectrum, which has been calculated corresponding to Lorentz, Gaussian and Voigt, respectively.

The Raman spectra of these superlattices reveal the relationship between the energy and the angle of the superlattice, which provides a reliable theoretical basis for the structure of the optoelectronic devices.

Figure 27: (A) Superlattice potential of graphene/h-BN. (B) The test spectrum of FWHM and λ_M as the function. (C) The test spectral line of different heterostructure by θ and R' as the function. (D) The Raman shift of h-BN/graphene superlattice with different calculated method [182].

3.3.5 Plasmon-phonon coupling and plasmon delocalization, high pressure and low loss of plasmons in graphene/h-BN heterostructure

High quality graphene/h-BN heterostructures including other two-dimensional materials are considered to have broad application prospects [183–186].

Figure 28A and B shows the SINS (synchrotron infrared nanospectroscopy) spectra of the graphene/SiO₂ and graphene/h-BN. From Figure 28A, the wavenumber at 765 cm⁻¹ belongs to a small additional band of G/SiO₂, which is the enhancement corresponding to the band at 1120 cm⁻¹ (red point line). In the Figure 28B, the wavenumber at 817 cm⁻¹ belongs to the longitudinal optical (LO) phonon of h-BN (green point line); the wavenumber at

1365 cm⁻¹ belongs to the transverse optical (TO) phonon of h-BN (green point line). On the other hand, there is a strength enhancement at 817 cm⁻¹, the same strength at 1365 cm⁻¹, respectively. The enhancement belongs to the transverse surface plasmons of graphene with the LO phonon band of h-BN. But, the coupling of plasmons-phonon polaritons has no effect on TO modes [186].

Compared with other metal materials, graphene has the unique property of strong field confinement and relatively low transport decay in the plasmons transport capacity [188–190]. Woessner et al. studied the propagating plasmons of high quality in graphene with h-BN by near-field microscopy and also do a quantitative study on the plasmon damping, which corresponds to the spectrum in Figure 28C and D [187]. From the figure, with the increase

Figure 28: SINS spectra of graphene/SiO₂ in (A) and graphene/h-BN in (B) [186], (C) and (D) are the spectral lines of plasmons damping in graphene/h-BN [187].

of the distance from the boundary of the heterostructure, the plasma damping decreases nonlinearly. The complex parameter ξ_{opt} , is made ordinate as shown in Figure 28C and D. The oscillating signal is fitted with equation 1:

$$\xi_{\text{opt}} = A \frac{e^{i2q_p x}}{\sqrt{x}} + B \frac{e^{iq_p x}}{x^a} \quad (1)$$

The attenuation of fringes away from the edge is caused by the combination of the damping and the geometric diffusion of the circular wave. The results show that the main damping is due to the intrinsic thermal phonons scattering in graphene and the dielectric loss in h-BN.

3.4 Potential applications of graphene/h-BN heterostructures in optical property

For graphene/h-BN heterostructures compared with the SLG and h-BN, the optical properties and photoelectric

properties have shown excellent performance, which has broad prospects in the application of optical devices and optoelectronic devices.

3.4.1 Light-harvesting devices (the potential applications in solar cell and photodetector)

Under the limitation of the current conversion efficiency standards, such as the Shockley-Queisser limit, the absorption of a single photon can only excite an electron in a conventional light harvesting device [172].

A device, using h-BN/graphene/h-BN heterostructures was prepared by Wu et al. [172], the schematics are shown in Figure 29A. Through experiments, the collection of multiple hot carriers in the six molar boron nitride semiconductor superlattice was investigated.

Figure 29A and C shows the results and optical images of the photonic collection device. Figure 29B shows a moiré

Figure 29: Anomalous photo-Nernst effect in graphene/BN superlattices [172].

(A) Schematics of device and photocurrent measurement. (B) The superlattices is made of graphene and h-BN. (C) Optical image of the device (A). (D) and (E) are the test results of device (A). (F) Typical spatially resolved scanning photocurrent map of the device (A).

pattern formed by graphene stack on the h-BN. Figure 29D shows the change of the resistance of the Dirac point and secondary Dirac point in the excitation field with the base graphite as the back gate and the longitudinal resistance as a function of 50 mT. When the back gate voltage is -4.7 and 4.4 volts, they correspond to two peaks, corresponding to the sPDs. A strong peak at the back gate voltage of -0.1 volts is the main Dirac point. Figure 29E is an image of the photocurrent variation corresponding to Figure 29D. Near the back gate voltage -4 and 4 volts, there is a phenomenon of photocurrent enhancement, corresponding to the electron and hole of secondary Dirac point position. The excitation laser is 660 nm. Figure 29F shows the device's scanning photocurrent image.

The use of graphene has been demonstrated by the photo-Nernst effect (which has been shown to absorb at least one of the five carriers of a photon), so that the zero-bias optical response is recorded at a 0.3 A/W . This phenomenon is due to the enhancement of the energy coefficient of the Lifshitz transition at the low energy Van Hov singularities. This electronic collection device provides an effective and flexible means for the fabrication of optoelectronic resonators and LED, based on the flexible optoelectronic devices of Van Der Waals heterostructure.

3.4.2 Light-emitting diodes

Withers et al., contrary to the conventional epitaxial heterostructures, stacked in the vertical direction by a mechanical transfer method [191–193], which interacts weakly with each other by the van der Waals force. Figure 30A is a simulation diagram of LED heterostructure; the heterogeneous structure is different from the traditional one as it contains only the semiconductor; they used as three different 2D materials: h-BN insulator, graphene metal, and transition metal sulfides with direct band gap (MoS_2). Figure 30B is a schematic diagram of the LED, which corresponds to Figure 30A TMDC, in which the electrons and holes pass through from the graphene layer tunnel through the h-BN dielectric layer to TMDC at the external bias. The inset is a physical image of LED corresponding to Figure 30A. Figure 30C is the comparison of PL MoS_2 monolayer, and EL spectra, it can be seen from the figure, the PL frequency is close to the frequency of EL around $V_b = 2.4$ V. After analysis, this phenomenon is the radiative recombination of X^- corresponding to the EL spectral line overlap.

In addition, the authors also show that the external emission efficiency of multilayer TMDCs LED is close to 10%, which is comparable to that of modern LED based

Figure 30: (A) The schematic of LED [192]. (B) The working principle diagram of LED [192] (the inset is the physical optical image). (C) The comparison diagram of PL and EL in single layer MoS_2 [191].

on organic materials. Although the wavelength of the LED heterostructure in the work of the single semiconductor from TMDCs range from 600 to 700 nm, it has the potential to extend the communication range of emission wavelength, and could reach the midinfrared band.

In fact, the authors attempted to make thin, transparent, and flexible polyester film LED. The main factors restricting the development of this technology are the lack of a scalable synthesis strategy for heterostructures. However, it is encouraging because simple Van Der Waals heterostructures have been proven to grow and the mechanics of two-dimensional layers of mechanical transfer have been made, suggesting that this barrier may eventually be overcome.

3.4.3 Solar cell

As the application of a low-cost photovoltaic, the structure of heterostructure based on graphene has become an excellent candidates for it [194–196].

Meng et al. [196] prepared the heterostructure using the CVD method. Figure 31A is the graphic illustration of graphene/h-BN/Si. Figure 31B shows that h-BN is employed in an effective electron blocking layer, which is inset in the graphene and n-Si. Owing to the wide band gap, h-BN can reduce recombination of the unfavorable carriers. With a negative electron affinity, ΔE_c of h-BN/Si is determined to be larger than that of Si (4.05 eV). The valence band offset ΔE_v is estimated to be less than 0.63 eV from the formula $\Delta \Delta E_v = E_g^{\text{hBN}} - E_g^{\text{Si}} - \Delta \Delta E_c$ by taking the room temperature band gaps of h-BN (5.80 eV) and Si (1.12 eV). The existence of small $\Delta \Delta E_v$ is also an important problem in avoiding the adverse effects of

the increase of the series resistance of the cell in the effective transmission of the hole from the silicon layer through the h-BN layer to graphene. On the other hand, they used two different methods for preparing the heterostructures, which are shown in Figure 31C and D. Figure 31E shows the J-V characteristics of different solar cells, which is a comparison of the spectral lines of the different structures prepared by the different methods corresponding to Figure 31C and D. From the comparison, we know that the heterostructure of the one-step method is better than that of the two-step method. The power conversion efficiency (PCE) of solar cell reaches 10.93%.

The layered h-BN is also used to improve the performance of the device. Because of its unique physical and chemical properties and the appropriate band structure, h-BN acts as an effective electronic barrier, hole transport, thus inhibiting the interface complex, so that the open circuit voltage significantly improved. On the other hand, based on h-BN, the carrier conductivity increases significantly and the resistance of the solar cell is reduced, which leads to the increase in the short-circuit current density. By improving the preparation method of the heterogeneous, the graphene/h-BN heterostructure can be directly grown, and the interface defect and contamination can be avoided, and the performance of the device can be greatly improved.

3.4.4 Nanoresonators (based on graphene/h-BN/ SiO_2 heterostructures)

The optical properties of graphene and h-BN have been changed due to graphene/h-BN heterostructures. In particular, the coupling between the surface plasmons

Figure 31: (A) Schematic diagram of solar cells. (B) Schematic diagram of working principle of solar cells. Schematic diagram of solar cells prepared by one step (C) and two step method (D). (E) Comparison of two methods for solar cell performance test J–V characteristics [196].

of the graphene and the phonons of h-BN leads to a new frequency-wavevector dispersion relation [95, 183–186].

Brar et al. [197] assembled graphene nanoresonators on a single layer h-BN nanosheet, which was used to measure the coupling between the plasmons and the excitons near graphene. They found that small mode volume and high modulus graphene plasma oscillator strengths of h-BN and the formation of two phonon coupling allows for strong coupling, thus forming the two clearly separated hybridization pattern show anticrossing behavior.

Figure 32A is the schematic of the nanoresonator based on graphene/h-BN heterostructure. The figure shows the schematic diagram of the motion of the graphene plasmons and the h-BN phonon under the laser excitation. The resonator is etched into an electron rod array pattern with a width ranging from 30 to 300 nm and a spacing ratio of 1:2. FTIR spectroscopy was used to measure the transmission mode with the vertical irradiation of nanoresonators, the test result is shown in Figure 32B, which is $1.0 \times 10^{13} \text{ cm}^{-2}$ carrier density. The wavenumber at 1370 cm^{-1} belongs to h-BN optical phonon, which the spectra lines below the Figure 32B. With the increase

in the width, the frequency has a significant red shift and the strength of the transmission modulation ($-\Delta T/T_{\text{CNP}}$) becomes higher. Figure 32C is the carrier-induced change in the transmission under different wavenumbers and energy of the same carrier density, which corresponds to Figure 32B. These features indicate that the h-BN optical phonon energy, which appears above and below the experimentally measured characteristics, and shows a strong inverse cross behavior pattern with a strong correspondence.

This work is based on graphene/h-BN heterostructure nanoresonator to test the graphene plasmons and h-BN phonon coupling results. However, the fabrication of the nanoresonator shows that the heterostructure has a broad prospect in the application of optoelectronic devices.

3.4.5 Photodetector and autocorrelator

Recently, 2D materials have shown a number of new properties, such as optical emission, parametric non-linearity, broadband ultrafast optoelectronic detection,

Figure 32: (A) Schematic of graphene nanoresonators. (B) Experimental device physical test line of nanoresonators. (C) Theoretical calculation spectrum corresponding to (B) [197].

saturable absorption, on-chip electro-optic modulation, etc. These unique properties make them an alternative to the optoelectronic platform for semiconductor devices [198–201].

A heterostructure consisting of a single layer of graphene encapsulated in a six party boron nitride, has high efficiency of photoelectric detection and ultrafast metrology [200]. Figure 33A is the structure of the photodetector. The illustration of the red circle is the side simulation of the heterogeneous structure formed by the encapsulation of SLG with h-BN. Figure 33B is the result of an electrical spectrum analyzer obtained by a high speed RF probe, with the measured power $\Delta f(V_{DS}=V_{GS}=0\text{ V})$. The measurement results show that the cut-off frequency of 42 GHz is 3 dB, and the results match the maximum velocity of the graphene photodetector. At the same time, the optical response of the zero drain source bias is also observed, a typical distinction between graphene and semiconductor high speed photodiode. Figure 33C is the delay time and the intensity of the optical current as the coordinates of the different input power, the change of the photocurrent image. From the figure, at $\Delta t=0$, the spectrum of the relaxation time and the width corresponds obviously to the sink.

The results of the measurement of photocurrent by using the gate voltage and drain source voltage as a function show that the thermal electrons mediate the photoelectric response. At the same time, the observed saturation photocurrent corresponds to the super collisional cooling mechanism of the electron phonon. This nonlinear optical response can be tuned to picosecond scale timing resolution on the optical on-chip autocorrelation measurements and extremely low peak power [201].

3.4.6 High-speed electro-optic modulator

Efficient, nanoscale, electro-optic modulator is an important part of optical interconnects. Due to the weak photoelectric effect of silicon, the silicon is a technical bottleneck in the modulator. As a substitute for silicon, graphene has special optical and electronic properties, which makes it an alternative to silicon-based materials in optoelectronic applications [202–204].

Based on the graphene/h-BN heterostructure and the silicon photonic crystal resonant cavity, Gao et al. integrated a high-speed graphene electro-optic modulator. There is a strong interaction between the light and the material in the submicron cavity, which makes the reflection of the resonator have high efficiency. After testing, the modulation depth is 3.2 dB, and the cut-off frequency is 1.2 GHz. Figure 34A is a schematic diagram of the structure of the electro-optic modulator, which the preparation based on the graphene/h-BN heterostructure. Double layer graphene capacitors on the quartz substrate coupled with a planar photonic crystal cavity. The gate voltage (V_G) is scanned slowly, and the optical response of the modulator is measured by observing the reflection spectrum of the cavity, as shown in Figure 34B. During the gate voltage increase in the range from 2.5 to 6.7 V, the carrier density of two graphene layers increased slowly. For the incident wavelength at 1551 and 1570 nm, there are two peaks corresponding to the carrier density, moreover, the intensity becomes suddenly stronger at $V_G=\pm 5\text{ V}$. Figure 34D shows the high speed response characteristics of the low-pass filter with a 3 dB cut-off frequency of 1.2 GHz. The RC time constant of the bilayer

Figure 33: (A) Schematic of the h-BN/SLG/h-BN photodetector on a buried silicon waveguide. The inset shows the electric field energy density of the fundamental TE waveguide mode, obtained by finite-element simulation. (B) High-speed response of the graphene photodetector. (C) Autocorrelation traces of the graphene-based autocorrelator with different input average power of the laser pulses [201].

graphene capacitors limits the cut-off frequency, which is consistent with the measurement of the impedance of the device.

This work shows that the electric adsorption of graphene can facilitate the powerful high performance electro-optic modulator in the photonic crystal cavity, with low energy consumption, told the wavelength scale mark, etc., wide broadband characteristics, which makes the equipment with high efficiency in photonic interconnection conversion, stability.

4 Summary and prospect

As a new 2D material, with very good optical and optoelectronic properties, graphene has an ultra-wide spectral response range, between the UV and the terahertz band to achieve full spectral response; as graphene has a high carrier mobility and ultra-fast optical response speed, it

is an ideal photoelectric material. However, the absorption rate of the SLG on the space incident light is only 2.3%, which greatly limits the potential of optoelectronics of graphene. At present, the optical absorption enhancement of graphene is a popular research area, and it is also a problem regarding graphene that needs to be solved in the field of optoelectronics.

A unique hexagonal lattice arrangement and the characteristics of the zero band-gap allow the electrons on the graphene to move freely, which gives graphene many extraordinary features. The 2D h-BN has a similar structure to the graphene lattice: wide band-gap electronic features make its chemical properties different from graphene, electrons will not easily flow in the boron nitride atoms, which basically is an insulator. The graphene has unique optical properties: SLG is approximately transparent, and has a broadband optical response throughout the light region, especially in the visible region, all of which make graphene suitable

Figure 34: (A) Schematic of modulator based on graphene/h-BN. (B) Cavity reflection spectrum as a function of V_G and wavelength λ . (C, D) The test spectrum of modulator with different parameter [204].

for use in next-generation optoelectronic devices and optical communication systems. Its excellent electrical conductivity and light transmission make it especially suitable for high-performance photoelectric detection equipment.

Hexagonal boron nitride has a zero optical response in the visible region; only in the deep ultraviolet region does it have an absorption peak. It is these two optical properties with almost different 2D materials, where the graphene interlayer lattice alignment aligned boron nitride lattice, a “super-lattice” was born, and the superlattice is what people pursue with the structure of high efficiency photoelectric properties. This feature is due to quantum mechanics and some unknown rules dominate the known interaction between particles, especially in the super lattice between the van Hough singular point detection of special quantum region. These high electron density regions are not available between the graphene layers or between the boron nitride layers. When high-energy

photons are directed to the superlattice, a high-energy photon can be converted into electrons in the van Hove singularity region, and these electrons, if collected by the electrodes, form a current. With this finding, researchers can create a more efficient device that allows more electronic feedback when photons are acquired. Future work will explore how to fuse the excited electrons into current for optimal energy conversion efficiency, and remove some of their superlattice annoying problems: such as the need for magnetic fields. We remain convinced that this efficient process between photons and electrons will bring significant progress.

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