

Research Article

Modification of the Band Gap of Hexagonal Boron Nitride in Contact with Graphene Through Systematic Annealing

Kenneth Kipkemoi Ketili^{*}, Simon Waweru Mugo, Richard Makori Onger

Department of Physics, Jomo Kenyatta University of Agriculture and Technology (JKUAT), Nairobi, Kenya

Abstract

Graphene/hexagonal boron nitride heterostructures provides an effective platform for tuning graphene's electronic and optical properties while preserving its inherently high carrier mobility. In this work, the effect of post-growth thermal annealing on the optical band gap of G/h-BN heterostructures is investigated to examine temperature-dependent modifications at the graphene–substrate interface. The optical response of the annealed heterostructures was characterized using UV–Vis spectroscopy over the spectral range of 200–800 nm. The absorption spectra reveal a systematic red shift of the absorption edge with increasing annealing temperature, indicating a progressive modification of the electronic structure. Tauc method was used in the approximation of the optical band gap where a reduction of the optical band gap from 2.86 eV for the lower annealing temperature to 2.17 eV at the highest annealing temperature was observed. This act is associated to thermally induced interfacial relaxation, including changes in stacking configuration, and moirés super lattice formation. These processes lead to a reduction in substrate-induced symmetry breaking in graphene, thereby influencing its optical transitions. The findings contribute to a better understanding of temperature-driven interfacial effects in van der Waals heterostructures and provide insights relevant to the development of graphene-based optoelectronic and thermoelectric devices designed to operate under varying thermal conditions.

Keywords

Graphene, Annealing, Stacking

1. Introduction

Over the past two decades since the discovery of graphene it has attracted intense experimental and theoretical interest thanks to its exceptional electronic, optical, and thermal properties [1, 8]. These include its extraordinarily high electron mobility arising from weak electron–phonon scattering. This has positioned graphene as a promising material for next generation electronic and optoelectronic applications [2]. Despite these outstanding properties, the performance of graphene based devices is often limited by substrate induced disorder.

A specifically effective way to overcome these limitations

is the integration of graphene with hexagonal boron nitride (h-BN) to form van der Waals heterostructures [1, 3]. Hexagonal boron nitride is a wide band gap insulating material with a hexagonal crystal structure, consisting of alternating boron and nitrogen atoms arranged in a two-dimensional honeycomb lattice [3, 9]. Graphene and h-BN possess closely matched lattice constants, with a lattice mismatch of only approximately 1.8%, making h-BN an ideal substrate for graphene. In contrast to conventional Silicon dioxide substrates, h-BN offers an atomically smooth surface, minimal charge trapping, and a

^{*}Correspondence: Kenneth Kipkemoi Ketili (kennethketili@gmail.com)

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low dielectric constant. As a result, graphene supported on h-BN exhibits significantly enhanced electronic quality which enables the observation of intrinsic properties that are otherwise suppressed by surface roughness and electronic inhomogeneity in Silicon dioxide supported graphene [4].

Apart from serving as a high quality substrate, h-BN can also induce new physical phenomena in graphene through the formation of moiré super lattices. The periodic potential arising from lattice alignment between graphene and h-BN leads to modifications in graphene's electronic and optical properties that do not occur in suspended graphene. From an optical perspective, previous studies have shown that oriented graphene/h-BN moiré heterostructures can enhance absorption in the infrared spectral range [5, 7]. While several reports have examined the overall optical response of graphene/h-BN heterostructures, the specific influence of the h-BN substrate on the intrinsic optical response of graphene in the visible spectral region remains insufficiently explored.

Concurrently, the effects of thermal treatment on the structural properties of graphene/h-BN heterostructures have been extensively investigated [6, 10, 11]. By controlling annealing temperature and graphene flake size, large-period moiré super lattices have been successfully engineered, indicating that thermal processing plays a crucial role in interfacial relaxation and structural reconstruction. Given the strong correlation between structure and optical response [12, 13], these findings suggest that thermal annealing may significantly influence the optical properties of graphene/h-BN heterostructures. However, experimental confirmation of this effect [14, 15], particularly in the visible spectral range, remains limited. In this work, we investigate the effect of post-growth thermal annealing on the optical band gap of graphene/hexagonal boron nitride (G/h-BN) heterostructures. The aim of this study is to highlight the potential of thermally engineered G/h-BN heterostructures for tunable optoelectronic and thermoelectric applications.

2. Methodology

G/h-BN/Si wafer 1 cm × 1 cm was sourced from Graphene supermarket USA, and it was prepared by Chemical Vapour Deposition as follows: A few-layer h-BN flakes were mechanically exfoliated from the synthesized h-BN nanocrystal 16 onto 100 nm SiO₂-coated Si substrate (Boron-doped). A monolayer graphene was then transferred onto h-BN sheet after Cu-catalytic CVD growth. Graphene growth began using CH₄ (300 Sccm) as precursor for 30 minutes after Cu pre-anneal process at 1000 °C. Once graphene monolayer was grown on Cu surface, polymethyl-methacrylate (PMMA) was spin-coated on one side of graphene and Cu was etched away using wet chemistry (FeCl₃ 6(H₂O) solution). After the PMMA (with graphene) was transferred onto the target substrate, it was removed with acetone and graphene monolayer positions itself on the target substrate where the location of h-BN flakes

is identified with Zeiss Axio 100 microscope and Motic microscope fitted with Motica 3.0. After acquiring the sample, it was cleaned using USP grade acetone to remove any impurities, and USP grade ethanol. Then rinsed using De-ionized water, and dried at standard room temperature in a vacuum oven. It was eventually stored at an air tight box.

2.1. Thermal Treatment of G/h-BN

A vacuum thermal annealing Oven (Drawell DZF-6210) was used.

The process temperature was increased up to the actual annealing temperature at a ramp-up rate of 6 °C/min.

The sample was annealed for 60 minutes at the actual annealing temperature, and then cooled down at an interval of 50 °C.

At 50 °C, the sample was removed from chamber to room temperature.

2.2. Optical Properties of G/h-BN

The transmittance spectra of G/h-BN in the UV-visible range was made using a spectrophotometer, (Shimadzu spectrophotometer type UV-1601 PC). The light source was generated by a halogen lamp. Then the light generated was passed through a monochromator and a 50:50 beam splitter before incident on the sample (G/h-BN) and the reference separately. The light intensity after passing through the absorptive materials was recorded by the detector. The intensity decay of the sample relative to the reference according to Lambert-beer law was plotted as either transmission or absorption against wavelength to obtain the spectral response of the Graphene on hexagonal Boron Nitride material.

3. Results

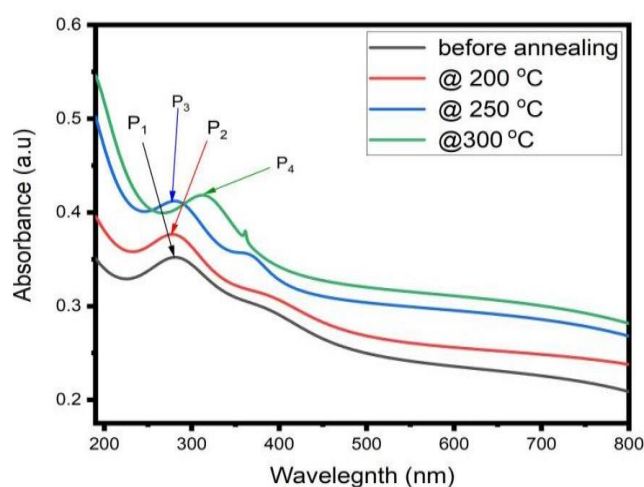


Figure 1. UV-visible absorption spectra of graphene/hexagonal boron nitride heterostructures before annealing and after annealing at 200°C, 250°C, and 300°C.

Figure 1 shows the absorption spectra of G/h-BN before annealing and after annealing at 200 °C, 250 °C, and 300 °C over the wavelength range of 200–800 nm. The un-annealed G/h-BN sample exhibits an absorption peak at approximately 281 nm and a weaker feature around 360 nm.

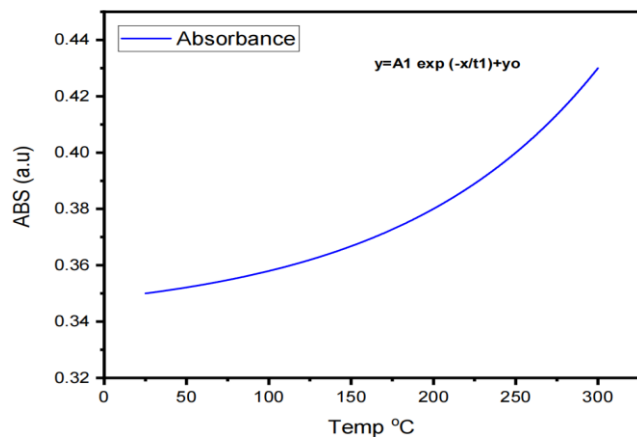


Figure 2. UV-VIS absorbance of G-hBN versus different temperatures.

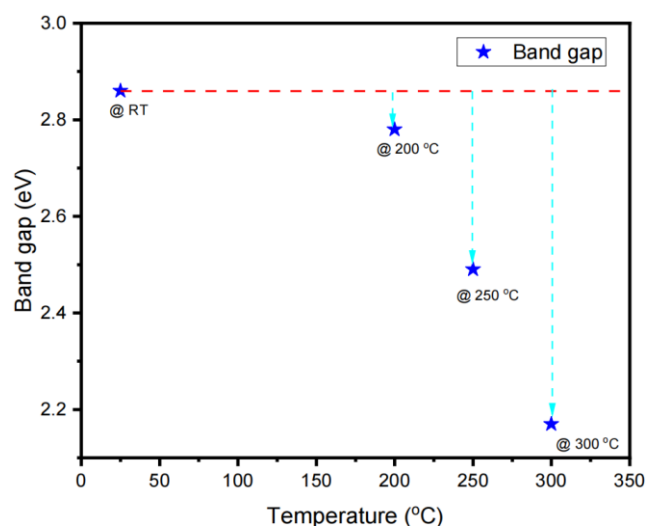


Figure 3. Variation of the optical band gap of graphene/hexagonal boron nitride (G/h-BN) heterostructures as a function of annealing.

The strong absorption in the ultraviolet region is attributed primarily to electronic transitions associated with h-BN, while the weaker feature in the near-UV region is consistent with Plasmon absorption in graphene. The non-monotonic shift in absorption wavelength with annealing temperature arises from competing effects of interfacial cleaning and strain relaxation at moderate temperatures (200 °C to 250 °C), followed by strain accumulation and defect activation at higher temperatures (250 °C to 300 °C). This red shift indicates a reduction in transition energy suggesting a temperature-induced modification of the electronic structure of the heterostructure. The

progressive nature of this red shift as is shown in Figure 2 implies that annealing alters the interfacial properties between graphene and h-BN rather than inducing abrupt structural damage.

The optical band gap values were extracted from the absorption data using the Tauc relation for indirect allowed transitions. Figure 3 presents the variation of the extracted optical band gap as a function of annealing temperature. The optical band gap decreases from 2.86 eV for the sample annealed at 200 °C to 2.17 eV for the sample annealed at 300 °C. This clear trend establishes a strong correlation between annealing temperature and band gap modulation.

The observed decrease in band gap with increasing annealing temperature suggests enhanced electronic delocalization within the graphene layer and a reduction in substrate-induced symmetry breaking.

4. Discussion

The observed reduction in the optical band gap of the graphene/hexagonal boron nitride heterostructure with increasing annealing temperature indicates a temperature-induced modification of the interfacial electronic structure. As much as graphene and h-BN interact primarily through van der Waals forces, there are theoretical and experimental evidence suggesting that any changes in interlayer distance, stacking configuration, and relative lattice orientation can significantly influence their electronic and optical properties. It is also in record that annealing can provide sufficient thermal energy to overcome local energy barriers, enabling structural relaxation and rotational alignment between graphene and the h-BN substrate. This process can induce the formation of moiré super lattices, which are highly sensitive to relative twist angle and stacking order. As reported in previous studies, different stacking configurations result in distinct interlayer distances and electrostatic environments, thereby altering orbital overlap and charge redistribution at the interface [7]. In A–A stacking, carbon atoms in graphene are positioned directly above boron and nitrogen atoms, leading to stronger orbital hybridization between graphene π states and h-BN valence states. This enhanced interaction increases sub lattice symmetry breaking in graphene, which theoretically results widening of the band gap [8]. While in A–B stacking, one carbon sub lattice aligns above boron atoms while the other aligns above hollow sites, producing a larger average interlayer distance and weaker orbital coupling. This configuration reduces sub lattice asymmetry which lowers the band gap [9]. The experimentally observed decrease in band gap with increasing annealing temperature in this work therefore suggests that annealing promotes a transition toward energetically favorable configurations with reduced interlayer interaction, most probably from A–A-like regions toward A–B stacking dominance. This interpretation is consistent with thermally induced graphene rotation reported in the literature, where annealing

drives the system toward lower-energy stacking configurations. These effects collectively decrease localized charge trapping and screening from the h-BN substrate contributing to the observed narrowing of the optical band gap. The red shift of the absorption edge with temperature also supports this conclusion, indicating enhanced delocalization of π electrons in graphene and reduced perturbation from the substrate.

5. Conclusion

The results demonstrate that even weak van der Waals interactions can be thermally tuned to engineer the electronic structure of graphene based heterostructures. The strong correlation between annealing temperature and band gap modulation highlights the potential of G/h-BN systems for temperature-sensitive optoelectronic and thermoelectric applications, where controlled band gap tuning is essential.

Abbreviations

UV-VIS	Ultraviolet- Visible
h-BN	Hexagonal Boron Nitride
G/h-BN	Graphene/Hexagonal Boron Nitride

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Author Contributions

Kenneth Kipkemai Ketili: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Resources, Software, Writing – original draft

Simon Waweru Mugo: Resources, Supervision, Validation, Visualization

Richard Makori Ongeri: Supervision, Validation, Visualization

Conflicts of Interest

The authors declare no conflicts of interest.

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