

The Challenges of Graphene Nanoribbons for MOSFET Channel

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Abstract: Graphene nanoribbon (GNR) has been reported as a solution for Graphene's zero bandgap problem as channel material for Metal Oxide Semiconductor Field Effect Transistor (MOSFET). By quantum confinement and atom engineering, GNR provides seemingly new hope for maintaining the advantages of Graphene while solving bandgap problems. However, GNR-based MOSFETs face a number of challenges that need to be addressed to fully utilize their potential. In this paper, we discuss the challenges associated with using GNR as the material for MOSFET channel.

Keywords: graphene nanoribbon, channel material, challenges, quantum confinement

1. Introduction

Channel materials play significant roles in metal-oxide-semiconductor field-effect transistors (MOSFETs), directly affecting the performance of the transistor. Silicon (Si) has traditionally been the primary material for channels. The strained-Si technology had already been the mainstream process beyond the 90 nm technology node [1-4]. However, as FETs are scaled down to nanometer dimensions, the significant limitations of Si-based materials have risen, including large gate dielectric thickness and pronounced short channel effects. Consequently, 2-dimensional (2D) materials have garnered interest, among which Graphene stands out as a competitive candidate.

Graphene, first produced in 2004, has received great attention in transistor area as its high mobility provide possibilities for high-efficiency field-effect transistors. It also has the advantage of less short channel effect compared to the traditional material Silicon. However, Graphene faces the fundamental problem: the absence of bandgap. To modify this material, many researches have been done on doping and quantum confinement, among which Graphene Nanoribbons (GNRs) were proposed as a promising solution.

Graphene Nanoribbons, the narrow strips of Graphene, are the achievements of quantum confinement. With ribbons of widths limited into nanometer scale, the motion of electrons is restricted to such narrow regions that their energy levels become quantized, which results in the formation of a bandgap—a distinct difference between the energy levels of the valence and conduction bands. For certain Graphene ribbons of a few nanometers in width, the band gap varies as a function of the ribbon

width. This means that a ribbon of width ~ 1 nm would be required to get the band gap of Silicon (~ 1 eV) [5,6], representing that its high on/off ratios are suitable for transistors.

Nevertheless, Graphene Nanoribbons still faces several significant problems unsolved, including the manufacturing problem, electrical performances as well as thermal and chemical instability. This paper aims to explore these challenges in detail, providing a comprehensive insight of the limitations of GNRs for MOSFET applications.

2. The formation and modulation of band gaps in GNR

2.1. How quantum confinement enables the formation of band gaps in GNR

Quantum confinement occurs when the dimensions of a material are reduced to the nanoscale, restricting the movement of electrons to a lower-dimensional space. The reduced width down to a few nanometers constrains electron motion to one dimension, creating a discrete set of energy levels. This effect results in an electronic bandgap that can be modulated by adjusting the ribbon width.

Due to quantum confinement effects, unlike Graphene with bandgap absence, Graphene Nanoribbons are able to exhibit energy band gaps. Using first-principles calculations, Son and et.al. found that both types of GNRs, Armchair Graphene Nanoribbons (AGNRs) and Zigzag Graphene Nanoribbons (ZGNRs), have direct, nonzero energy gaps that decrease as ribbon width increases. [7] This inverse correlation enables the prediction of band gap energy from the ribbon width. From theoretical calculation, the width of around 1 nanometer is required to reach the band gap energy of Silicon. [5,6] However, the production of GNR smaller than 10 nm remains a significant challenge.

2.2. The atomically bottom-up fabrication of GNRs of ideal widths

As an optimistic update, Cai and et.al. introduced an atomically precise bottom-up fabrication of GNR, enabling the production of sub-10 nm GNRs. This approach employs molecular precursors to precisely control ribbon width and edge structure, allowing for the fabrication of very narrow GNRs with widths around 1–2 nm. This proposed method thus provides a promising possibility for producing GNRs at ideal widths. [8]

3. Electronic performances of GNR

3.1. How can we define an ideal performance of GNR

In order to discuss the electrical performance of GNR as channel material, we should firstly make comparisons. We compare several properties of GNR with that of silicon. Silicon, as the most widely used semiconductor material in electronic circuits, possesses very excellent physical properties[9-13]: a moderate bandgap width (1.1 eV), a huge resistivity controlled by doping and concentration (where high-purity silicon is approximately 2.3×10^3 k $\Omega \cdot$ cm), a relatively high carrier mobility ($\mu_n=1400$ cm²/V $\cdot$ s, $\mu_p=450$ cm²/V $\cdot$ s), and a high thermal conductivity (single-crystal silicon $k=150$ W/m $\cdot$ K). While in comparison, graphene itself has an extremely high mobility (2×10^5 cm²/V $\cdot$ s), a Young's modulus of 1 TPa, and an inherent strength of 130 GPa, but also because it has high thermal conductivity ($k=3000$ W/m $\cdot$ K)[14-16]. While in terms of bandgap problem, through critical process, ideal bandgap can be created when the material is confined into several atoms wide. The bandgap of some of the GNR is listed in the table (table 1) [17]

Table 1: Bandgaps of several GNRs (Hao Luo and Gui Yu Chem. Mater. 2022, 34, 3588–3615)

GNR type	backbone/edge type	bandgap size/eV
7-AGNR	armchair edge	2.6
B-doped 7-AGNR	armchair edge	0.8
CN-doped 7-AGNR	armchair edge	1.5/1.6 ^a
10-AGNR	armchair edge	2.0
13-AGNR	armchair edge	1.4
S-doped 13-AGNR	armchair edge	1.5
9-AGNR	armchair edge	1.4
N-doped 9-AGNR	armchair edge	2.7
18-AGNR	armchair edge	0.9
21-AGNR	armchair edge	0.7
5-AGNR	armchair edge	0.1
8-AGNR	armchair edge	1.0/2.3 ^b
11-AGNR	armchair edge	0.2 ^d
14-AGNR	armchair edge	0.2
14-AGNR QD	armchair edge	
6-ZGNR	zigzag edge	1.5/1.9 ^c
9-zeeGNR	zigzag edge	1.4
17-zeeGNR	zigzag edge	0.9 ^d
NBN-edged ZGNRs	zigzag edge	1.5/0/8 ^e
6/9-CGNR	chevron edge	1.6
(3,1)-chGNR	chiral edge	0.7
(4,1)-chGNR	chiral edge	0.5 ^d
OBO-edged (4,1)-chGNR	chiral edge	3.3

As commonly used channel material silicon has the bandgap of 1.12eV, while highly anticipated wide bandgap semiconductors GaN and SiC have bandgap of 3.39eV and 3.23eV, quantum confinement does enable graphene to gain manageable semiconductor property with different width.

3.2. Balancing bandgap with mobility

However, while creating a usable bandgap, there remains an inverse relationship between bandgap and mobility. Jinying Wang et.al [18] has discussed such inverse relationship in their work. As stressed, the mobility of one-dimension material can be written into following formulation:

$$\mu = \frac{e\bar{v}^2}{(2\pi k_B T)^{1/2} |m^*|^{3/2} E_1} \quad (1)$$

Where e is the electron charge, $\bar{v}$ refers to the average velocity, k_B is the Boltzmann constant, T is the temperature, m^* refers to the effective mass, E_1 is the deformation potential constant. The linear relationship between effective mass m^* and bandgap E_g can be written into:

$$m^* = \frac{2\hbar^2}{9t_0^2 r_0^2 E_g} \quad (2)$$

Where t_0 is the transition parameter, r_0 is the equilibrium bond length, and $\hbar$ is the reduced Planck constant. Then the expression of deformation potential constant E_1 is related to the strain dependence of Fermi level E_F and bandgap E_g :

$$E_1 = \frac{\partial E_{edge}}{\partial \epsilon} = \frac{\partial E_F}{\partial \epsilon} \pm \frac{1}{2} \frac{\partial E_g}{\partial \epsilon} \quad (3)$$

Where ϵ is the strain. In the formulation, the relying relationship between bandgap E_g and strain ϵ can be written into:

$$\frac{\partial E_g}{\partial \epsilon} = \pm 3t_0 S_t (1 + \nu_A) \quad (4)$$

Where S_t is a constant that reflects the dependence of transition parameters on bond length, where ν_A is Poisson's ratio. Combining all the formulations above, we finally get:

$$\mu = \frac{27et_0^3r_0^3c}{(16\pi k_B T)^{1/2} \hbar \left(\frac{\partial E_F}{\partial \epsilon} \pm 3t_0 S_t (1 + \nu_A) \right)^2 E_g^{3/2}} \quad (5)$$

This indicates that with bandgap E_g increases, the mobility μ is decreasing with the relationship of negative two-thirds power. This is mainly because as the bandgap being created, the effective mass m^* also increases. Effective mass is one of the key factors affecting carrier mobility. The larger the effective mass, the lower the ability of carriers to accelerate under the action of an electric field, resulting in a decrease in mobility. Besides, phonon scattering also plays an important role. At room temperature, phonon scattering is one of the main factors limiting the intrinsic mobility of graphene. When the bandgap is opened, the effective mass of charge carriers increases, leading to an increased probability of scattering with phonons and a decrease in mobility.

However, Wang also provides possible ways for balancing such inverse relationship. The deformation potential constant E_1 also has a significant impact on mobility, and its value depends on the dependence of the Fermi level and bandgap on strain. Through strain engineering, E_1 can be adjusted to change the transmission polarity of AGNRs, providing the possibility of achieving high mobility and large switching ratio. [18] More research based on the area are demanding.

4. Instability problems of GNR

4.1. Unpredictability Issues with GNR

The properties of graphene nanoribbons are significantly influenced by their structure. Graphene can be classified into two categories according to the cut edge shapes: zigzag edges and armchair shapes. The armchair form may have semiconducting or metallic properties, depending on its width, whereas the zigzag edges are anticipated to have metallic properties using tight-binding approximation model calculations. [19-20] Nevertheless, the armchair shape has semiconducting properties with an energy gap that is inversely correlated to the nanoribbon width, according to calculations based on density-functional theory. According to experimental findings, the energy gap widens as the nanoribbon width decreases. [21-22] Despite having beneficial characteristics in theory, both varieties of graphene nanoribbons are catastrophically unstable in real-world applications, particularly when scaled down to the nanoscale. Furthermore, one significant element influencing the performance of graphene nanoribbons as channel materials is their interaction with the substrate.

4.2. Fatal instability based on graphene nanoribbon structure

4.2.1. Instability of zigzag graphene nanoribbons

Some of the most appealing aspects of the GNR depend on the serrated edge segments, which, unlike armchair edges, are not chemically stable enough to tolerate exposure to air, even for structures with a largely closed shell. [23-24]

Because of the confined states created at the edges, sawtooth GNRs show comparatively high energy instability. Electron mobility may be reduced as a result of these localized states' ability to

encourage electron recombination. According to experimental research, these instabilities sharply rise and ultimately result in material failure when the GNR's width is decreased to a particular extent.

4.2.1.1. Manifestations of Instability

Local edge status: The edge of the sawtooth is introduced to the local electronic status at the edge of the nanopal. There may be unpaired electrons in these edge states to generate magnetic torque. Due to these magnetic torque, jagged graphene nanofiber (ZGNR) shows the ferromagnetic.

Magnetic phase: ZGNR may display a ferromagnetic phase where a net magnetic moment is produced by the parallel alignment of the magnetic moments. Armchair graphene nanoribbons in an edge-free condition, on the other hand, do not show the same magnetic activity.

Size dependence: ZGNR's breadth and length may have an impact on its magnetic characteristics. A weakening of the magnetic moment could result from the edge state being less defined as the nanoribbon's width expands. Conversely, higher magnetic characteristics are frequently displayed by thinner nanoribbons. [25-26]

4.2.1.2. Instability mechanisms

The following factors are the main reasons for the instability of jagged edge graphene:

Effect of edge states: Unsaturated bonds at zigzag edges can react with nearby molecules, creating defects and degrading the material's electrical properties.

Environmental factors: Changes in temperature, humidity, and chemical environment can cause phase transitions and degradation of zigzag edge graphene properties.

Material imperfections: Lattice defects that may arise during synthesis may make inhomogeneities in material properties worse.

4.2.1.3. Improvement measures

The following strategies can be considered to improve the stability of zigzag edge graphene:

Surface modification: Enhance the antioxidant and water vapor resistance of serrated graphene by using chemical modification techniques to reduce the influence of the environment on its stability.

Application of composite materials: Composite serrated graphene with other materials to improve the overall performance and environmental adaptability.

The zigzag edge's structure enhances its edge effect, resulting in enhanced localization of electrons and thus improving its electron transport properties. However, this structure is more likely to be unstable under mechanical stress compared to flat graphene ribbons.

Due to the presence of jagged edges, localized stress concentrations may lead to cracking or yielding of the material, which in turn affects the overall structural stability. Such sharp edges have an impact on the mechanical strength of the material and may make it more vulnerable to external stresses.

4.2.2. Instability of armchair graphene nanoribbons

A structure of graphene is an armrest chair structure. In some cases, it has a special geometric shape and can make it higher stability. When external interference, this structure can help the material decentralized stress more effectively. However, the armchair structure has the same shortcomings as the tortuous edge structure, because the local stress in folding and edges will still cause the material unstable, especially in high pressure or high temperature environment. The armchair GNR is easily affected by the environment, especially in the case of oxygen and moisture. These factors may cause chemical reactions, such as oxidation, which may damage performance.

The bottom -up method can adjust the width and edge of the graphene nano fiber (GNR) on the edge of the armchair. This allows precise adjustments to the electronic band. This allows accurately adjusting optical response and electronic band gaps by changing the structure and coupling mode of the molecular building block. [27-28]

4.2.2.1. Structural properties of armchair graphene

Different electronic characteristics of the armchair petrochemical are formed by a parallel chain of the carbon atom that constitutes its crystal structure. Its semiconductor characteristics are determined by the intersection of its price and conduction band. In some cases, the handrail chair graphene has a high conductivity than graphene with a sawtooth -shaped edge, but it is also more vulnerable to external affected.

4.2.2.2. Manifestations of Instability

Thermal instability

The thermal vibration of the armchair at high temperature may destroy the carbon bond, which produces structural instability. This phenomenon is very obvious in high -power electrical equipment.

Electric field effects

The electronic distribution in graphene can be changed through an external electric field, resulting in non -uniform non -carrier concentration. Conversely, this will lead to a decline in electronic migration and conductivity.

Chemical environment

The handrail chair graphene may go through the oxidation process under chemical conditions including oxygen and water vapor, which may lead to forming surface defects and changing its electrical characteristics.

4.2.2.3. Mechanisms of instability

The following elements are mainly related to the instability mechanism:

Quiet defects: These defects can cause local stress concentrations and reduce the overall stability of the material during synthesis and use.

Environmental factors: Phase changes and modifications in the electrical properties of materials can be achieved through changes in the external environment (including temperature, humidity, and electric field).

Chemical reactions: The chemical properties of graphene's surface can change due to interactions with surrounding molecules, which can affect the material's ability to conduct electrons.

4.3. Substrate interactions and substrate requirements when using GNR as a channel material

4.3.1. Interaction

Van der Waals forces: One of the key elements causing graphene nanoribbons and the base material to come into physical contact is the van der Waals force between them. The structural stability and morphological integrity of the nanoribbons depend on this interaction.

Chemical bonding: The overall performance of the device will be impacted by the electron transport at the interface if the substrate material may undergo a chemical reaction with the graphene nanoribbons. For instance, specific metal substrates may cause charge carriers to localize, changing the graphene nanoribbons' conductivity.

Electrostatic interactions: Graphene nanoribbons' energy band structure is influenced by the substrate's charge distribution, which in turn modifies their conductivity. The electrical interaction can be realized by applying a gate pressure that induces different carrier concentrations on the graphene nanoribbons.

4.3.2. Requirements for the substrate

Low loss and high transparency: The substrate material should have low electron loss and good optical transparency to facilitate the transmission and absorption of light in the optoelectronic device.

Good thermal conductivity: Graphene nanoribbons have very high thermal conductivity, and the substrate material needs to have good thermal conductivity to effectively dissipate heat and ensure the stability of the device under high load.

Chemical inertness and high stability: The substrate must have excellent chemical inertness and stability to avoid unnecessary chemical reactions with graphene nanoribbons.

Appropriate surface roughness: The surface structure of the substrate should be smooth to reduce scattering and the introduction of defects, while the roughness can be appropriately adjusted to optimize the fixation and stability of graphene nanoribbons.

Insulating or semiconducting properties: In some application scenarios, the substrate should be an insulator to prevent charge leakage or a semiconductor to enable electrical performance tuning.

The performance of Graphene Nanoribbons is significantly affected by the substrate material. In order to achieve efficient device performance, the interaction mechanisms between Graphene Nanoribbons and the substrate must be thoroughly investigated and a suitable substrate must be selected based on these mechanisms.

5. Manufacturing difficulty of GNR

The manufacturing difficulty of graphene nanoribbons (GNR) is mainly reflected in the complexity of the preparation process, the high cost, and the challenge of controlling the size and shape.

The preparation of GNR requires specific chemical reactions or physical processes, such as chemical vapor deposition (CVD), lithography, etc. These processes are often complex and require precise parameter control, such as reaction time, temperature, and pressure. The raw materials and equipment needed for preparing GNR are usually expensive, especially when using high-purity carbon sources and specialized equipment. Additionally, the yield during the preparation process may not be high, which further increases the cost. During the preparation of GNR, it is easy to introduce surface defects, such as vacancies and dislocations. These defects can significantly affect the electronic properties and mechanical strength of GNR. Therefore, how to reduce surface defects is a major issue in the preparation process. After the preparation process, there may be impurities mixed in the GNR, such as residual metal catalysts and other carbonaceous substances. How to effectively remove these impurities while ensuring that the structure of GNR is not damaged is also an important issue to be solved.

5.1. The difficulty of large-scale synthesis

The essential prerequisite for the large-scale integration of graphene materials is the synthesis of high-quality graphene with large areas and controllable thickness. Graphene was first discovered and obtained through a process involving adhesive tape-assisted mechanical exfoliation. The current approach yields graphene flakes of superior quality in terms of purity, defect minimization, carrier mobility, and optoelectronic performance. Besides, many efforts have been made to produce high quality graphene, such as liquid phase exfoliation [27], chemical vapor deposition (CVD) [28], annealing of carbon-containing substrates [29], and reduction of graphene oxide. [30] The large-scale

synthesis of graphene nanoribbons presents numerous challenges, including the complexity of preparation processes, high costs, difficulties in controlling size and shape, surface defects, and purification issues. Addressing these challenges through innovative synthesis methods, automated manufacturing, post-synthesis treatments, green approaches, and collaborative R&D efforts is essential for advancing GNR technology towards commercial viability. By overcoming these obstacles, the full potential of graphene nanoribbons in various cutting-edge applications can be realized.[31]

5.2. Technological requirements of supporting material (with silicon dioxide substrate no longer satisfying)

Despite their potential, the transition from laboratory-scale synthesis to large-scale production faces numerous obstacles. Silicon dioxide (SiO_2), traditionally used as a substrate for GNR synthesis, has limitations that hinder its effectiveness in large-scale applications. Silicon dioxide substrates have limitations in terms of thermal conductivity, electrical insulation, and compatibility with high-temperature processes. Novel substrates such as hexagonal boron nitride (h-BN) or transition metal dichalcogenides (TMDs) offer improved performance characteristics suitable for large-scale GNR synthesis.[32]

Supporting materials must exhibit high thermal conductivity to manage the heat generated during synthesis effectively. This helps in maintaining optimal reaction conditions and preventing thermal degradation of the GNRs. Good electrical insulation properties are crucial to prevent undesired current leakage and interference during the synthesis process. Substrates with low dielectric constants and high resistivity are preferred. Advanced substrates should have smooth and uniform surfaces to facilitate the growth of high-quality GNRs. Surface roughness and defect density must be minimized to ensure consistent nucleation and growth.

Atomically thin graphene cannot maintain large-area self-support, so a supporting layer is usually used to protect graphene from structural damage during the transfer process [33]. Currently, polymer thin films are widely used as the supporting layer for transferring graphene. The criteria for selecting polymers include: (i) sufficient mechanical strength and suitable flexibility; (ii) good adhesion with graphene and the transfer medium; (iii) high resistance to chemical solutions during the transfer process; (iv) completely removable without residues. Since 2008, PMMA has become the most used supporting layer for the transfer of CVD-grown graphene [34].

6. Conclusion

In summary, Graphene Nanoribbons show great potential as MOSFET channel materials, especially in the field of high-performance electronic devices. However, its application still faces many challenges, including the complexity of the preparation process, the difficulty of bandgap modulation, the interfacial compatibility problem with other materials, and the stability under actual operating conditions. These factors limit the widespread application and commercialization of Graphene Nanoribbons.[35] Llinas and et.al have reported the performance of present Graphene Nanoribbon transistors. As stressed, the performance is far from ideal enough to replace traditional transistors not only because the bandgap problems but also because of the Schottky Barrier arising from the substrate interference. Besides, the bias voltage and control current are still not usable in real circumstances.

Therefore, more researches on chemical, physical and material engineering are required. Future research should focus on optimizing preparation techniques, exploring novel doping methods, and enhancing the regulation of material interfaces. Only through continuous innovation and cooperation can the advantages of Graphene nanoribbons be fully utilized to realize their application in MOSFETs and promote the progress and development of electronic device technology.

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