

## 石墨烯外延生长及其器件应用研究进展

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**摘要:** 石墨烯具有优异的物理和电学性能, 已成为物理和半导体电子研究领域的国际前沿和热点之一. 本文简单介绍了石墨烯的物理及电学特性, 详细评述了在众多制备方法中最有希望实现石墨烯大面积、高质量的外延生长技术, 系统论述了不同 SiC 和金属衬底外延生长石墨烯的研究进展, 并简要概述了石墨烯在场效应晶体管、发光二极管、超级电容器及锂离子电池等光电器件方面的最新研究进展. 外延生长法已经初步实现了从纳米、微米、厘米量级石墨烯的成功制备, 同时可实现其厚度从单层、双层到少数层的调控, 有望成为高质量、与传统电子工艺兼容、低成本、大面积的石墨烯宏量制备技术, 为其器件应用奠定基础.

**关键词:** 石墨烯; 外延生长; 器件; 进展; 综述

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## Epitaxial Growth of Graphene and Their Applications in Devices

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**Abstract:** Due to its outstanding physical and electrical properties, graphene has become one of the hot research topics and frontiers in the fields of physics and semiconductor electronics. The physical and electrical properties of graphene were briefly introduced. A comprehensive review was presented to the current research activities concentrated on the epitaxial growth of graphene which could be the most promising strategy among the reported methods to meet the challenge for mass production of graphene with high quality. A systematical discussion was then presented to the epitaxial growth of graphene by using various substrates of SiC and metals. By the end of this article, an overview was made on the recent applications of graphene in opto/electronic devices, such as field-effect transistors, light emitting diodes, supercapacitors and lithium-ion batteries. It is accepted that not only growth of graphene with sizes from nanometer to centimeter could be achieved, but also the thicknesses with monolayer to a few layers could be successfully tailored via epitaxial growth of graphene on SiC/metal substrates. It is promised that the strategy of epitaxial growth could accomplish the mass production of graphene with high quality, low cost and compatibility to the conventional electronic process, which lays the significant foundations for the applications of graphenes in devices.

**Key words:** graphene; epitaxial growth; devices; progress; review

2004 年, 英国 Manchester 大学的安德烈·海姆和康斯坦丁·诺沃肖洛夫<sup>[1]</sup>通过胶带剥离(亦称微机械

力分裂法: Microfoliation)高定向石墨, 首次制备出独立存在的、只有一个原子层厚度的二维晶体结构

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—石墨烯. 它推翻了“完美二维晶体结构无法在非绝对零度下稳定存在”的定论, 开启了一扇基于二维体系的理论和实验研究大门. 石墨烯因其晶体和电子结构而具有独特的物理现象, 被认为是未来新一代的半导体材料, 在高性能纳电子器件、复合材料、场发射材料、气体传感器及能量存储等领域具有广阔的应用前景.

## 1 石墨烯基本特性

Partoens 等<sup>[2]</sup>研究发现, 当石墨的堆垛原子层数少于10个单原子层时, 石墨层就会具有与普通三维石墨不同的电子结构. 一般将10层以下的石墨结构统称为石墨烯. 单层石墨烯的晶体结构如图1(a)所示<sup>[3]</sup>, 是由碳六元环组成的二维(2D)周期蜂窝状点阵结构, 厚度只有0.335nm, 相当于头发丝直径的1/200000. 它可以翘曲成零维(0D)的富勒烯(Fullerene)(图1(b)), 卷曲成一维(1D)的碳纳米管(Carbon Nanotube, CNT)(图1(c))或者堆垛成三维(3D)的石墨(Graphite)(图1(d)). 因此, 石墨烯被认为是构成其它碳材料的基本单元.

### 1.1 力学特性

石墨烯是目前已知最薄的材料, 厚度仅有0.335nm. 其C—C键仅为0.142nm, 石墨烯中的每个碳原子与其它3个碳原子通过强 $\sigma$ 键相连<sup>[4]</sup>, C—C键( $sp^2$ )使其成为已知最为牢固的材料之一. 它比钻石还坚硬, 强度比钢铁高100倍. 石墨烯内部的碳原子之间的连接很柔韧, 当施加外力于石墨烯时, 碳原子面会弯曲变形, 使得碳原子不必重排以适应外力, 从而保持结构的高稳定性. 迄今为止, 尚未发现石墨烯中有碳原子缺失的情况, 即六边形晶格中的碳原子均未丢失或发生移位. 稳定的晶格结构还

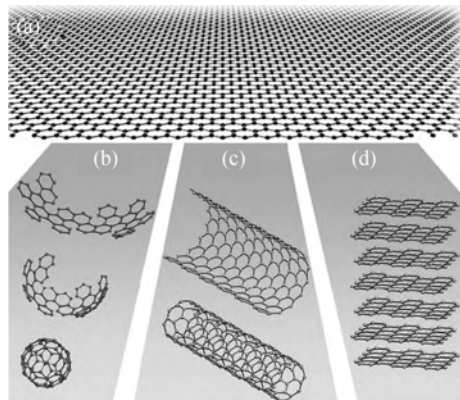


图1 (a)石墨烯, (b)富勒烯, (c)碳纳米管, (d)石墨的晶体结构<sup>[3]</sup>  
Fig. 1 Crystal structure of (a) graphene, (b) fullerene, (c) carbon nanotube and (d) graphite<sup>[3]</sup>

赋予了石墨烯优异的导热性. 石墨烯因其优异的力学特性(石墨烯的力弹性系数为 $10^5\text{N/m}$ , 杨氏模量达 $0.5\text{TPa}$ <sup>[4]</sup>), 有望解决微型处理器制造过程中所遇到的压力问题, 再加上其出色的电子特性, 有望成为未来制造微型处理器的首选材料<sup>[5]</sup>.

### 1.2 电学性质

碳原子有4个价电子, 其中3个电子生成 $sp^2$ 键, 即每个碳原子贡献一个未成键的电子位于 $p_z$ 轨道, 近邻原子的 $p_z$ 轨道与平面成垂直方向形成 $\pi$ 键, 为半填满状态, 电子可在二维晶体内自由移动, 因此石墨烯具有良好的导电性<sup>[6]</sup>. 其电子以光速的1/300移动, 具有相对论粒子特性<sup>[7]</sup>, 并可不用通过散射而进行亚微细距离移动, 使得隧道单分子晶体管的设想成为现实. 另外, 其电子在轨道中移动时, 不会因晶格缺陷或引入外来原子而发生散射. 鉴于原子间作用力十分强, 在常温下, 即使周围碳原子发生挤撞, 石墨烯内部电子输运受到的干扰也非常小. 它的电子迁移率在室温下可以超过 $15000\text{cm}^2/(\text{V}\cdot\text{s})$ <sup>[7]</sup>, 即使在电场引起的非平衡载流子浓度非常高的情况下, 其迁移率依然保持一个很高的值; 而且, 研究表明单层石墨烯中载流子的迁移速率受温度及化学掺杂的影响很小<sup>[8]</sup>. 石墨烯的价带( $\pi$ 电子)和导带( $\pi^*$ 电子)相交于费米能级处(K和K'点), 即形成所谓狄拉克锥结构(Dirac cones)(图2), 是能隙为零的半导体, 为目前已发现的电阻率最小的材料. 在费米面附近的传导电子( $\pi$ 键电子)具有线性色散关系<sup>[7,9-10]</sup>, 这导致了石墨烯在费米面附近的传导电子遵从相对论量子力学中的有效质量为零的Dirac方程<sup>[10-11]</sup>, 成为凝聚态物理学中验证相对论理论及无质量狄拉克费米子的天然理想模型. 石墨烯独特的载流子特性和无质量的狄拉克费米子属性使其能够在室温下观测到霍尔效应<sup>[12]</sup>. 另外, 石墨烯还具有量子隧道效应及半整数霍尔效应<sup>[13]</sup>、安德森局域化的弱化现象、永不消失的电导率等特性.

此外, 石墨烯还具有其它一些优异的物理化学特性, 如高吸附性、高化学稳定性, 高达 $2630\text{m}^2/\text{g}$

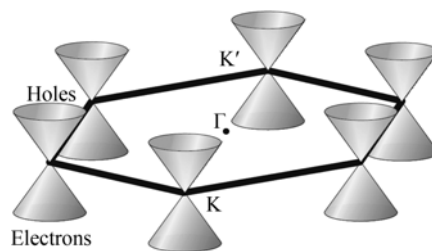


图2 石墨烯费米能级附近的能带结构<sup>[9]</sup>  
Fig. 2 Band structure of graphene in the vicinity of Fermi level<sup>[9]</sup>

的理论比表面积<sup>[14]</sup>、铁磁性<sup>[15-16]</sup>、良好的导热性 $(3080\sim 5150\text{W}/(\text{m}\cdot\text{K}))$ <sup>[17]</sup>等. 最近研究发现, zigzag 边缘的石墨烯还具有光致发光现象<sup>[18-19]</sup>. 这些优良性质不仅为凝聚态物理和量子电动力学提供了较好的研究平台, 还使其有可能替代 Si 材料而成为新一代计算机芯片材料, 具有广泛的应用潜力.

## 2 石墨烯的制备

自海姆等采用胶带剥离法制得石墨烯以来, 新的石墨烯的制备方法层出不穷, 如: 化学剥离法<sup>[20]</sup>、化学刻蚀法<sup>[21]</sup>、离子体刻蚀法<sup>[22]</sup>、电化学法<sup>[16]</sup>、电弧法<sup>[23]</sup>、溶剂热法<sup>[24]</sup>等. 然而, 低成本、大面积、高质量的石墨烯的宏量制备技术仍是当前此领域所面临的主要困难和挑战. 据文献报道, 其制备方法大致可分为物理法和化学法两大类. 鉴于已有对石墨烯胶带剥离和氧化石墨还原制备的综述报道<sup>[25-30]</sup>, 本论文将侧重评述石墨烯的外延生长.

所谓外延法, 即在一个晶体结构上通过晶格匹配生长出另一种晶体的方法. 与其它制备方法相比较, 外延法是最有可能获得大面积、高质量石墨烯的制备方法. 所获得的石墨烯具有较好的均一性, 且与当前的集成电路技术有很好的兼容性, 因此成为石墨烯制备科学的研究前沿与热点, 已列为我国 2011 年重大科技研究计划之一. 根据所选基底材料的不同, 外延法一般分为 SiC 外延法和金属外延法(均属异质外延).

### 2.1 SiC 外延法

早在 20 世纪 90 年代中期, 人们就已发现 SiC 单晶加热至一定的温度后, 会发生石墨化现象. SiC 单晶外延生长石墨烯的基本工艺如下: 首先把经过氧化或  $\text{H}_2$  刻蚀处理过的 SiC 单晶片置于超高真空和高温环境下, 利用电子束轰击 SiC 单晶片, 除去其表面氧化物; 然后在高温条件下将其表面层中的 Si 原子蒸发, 使表面剩余的碳原子发生重构, 即可在 SiC 单晶片表面外延生长石墨烯. 简单地说, 就是通过超高真空高温加热单晶 SiC 脱除 Si, C 原子重构生成石墨烯片层. 当对其工艺参数进行调控, SiC 外延法还可实现单层<sup>[31]</sup>和多层石墨烯<sup>[32]</sup>的可控制备. SiC 外延生长石墨烯所用到的 SiC 单晶基片包括 6H、4H、3C 等晶型, 其研究进展概况如表 1 所示.

SiC 外延法在技术上有一定优势, 可得到单层或少数层较为理想的石墨烯(如图 3 所示), 且 SiC 本身就是一种性能优异的半导体材料, 与目前的 Si 基

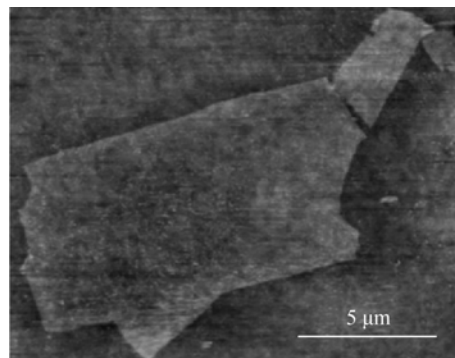


图 3 SiC 外延单层石墨烯 AFM 图<sup>[48]</sup>

Fig. 3 AFM image of graphene monolayers epitaxial growth on SiC substrate<sup>[48]</sup>

半导体工艺相兼容(不需要转移), 因此这种方法生长的石墨烯是最有可能实现 C 基集成电路的有效途径之一(图 4). 其缺点是: 目前还难以实现大面积制备、能耗高、不利于后续石墨烯的转移(需要转移的时候, 很难做到只腐蚀基底 SiC 而不破坏石墨烯结构).

### 2.2 金属表面外延法

采用与石墨烯晶格匹配的金属单晶体为基底(如 Ru(0001)、Ni(111)、Ir(111)、Pt(111)等), 在高真空环境中, 热解含碳化合物(例如: 乙烯、乙炔、苯、吡啶等), 通过调控和优化制备工艺参数, 石墨烯可望均匀铺满整个金属基底, 达到大面积制备的目的, 在亚原子单层的沉积速率控制下, 可望获得高质量近零缺陷的石墨烯. 金属外延法基本特点是: 所制备的石墨烯大多具有单层结构, 能够生长连续、均匀、大面积的单层石墨烯, 因此其研究已经成为当前的研究热点之一. 较之 SiC 外延法, 金属外延的石墨烯还具有易于转移的优点(通过化学腐蚀去掉金属基底). 其基本生长机理如下: 在高真空/ $\text{H}_2$  气氛条件下, C 和金属的亲合力比 Si、N、H 和 O 等元素的高, 因而 Si 和 H 元素均可被脱除, 而溶解在金

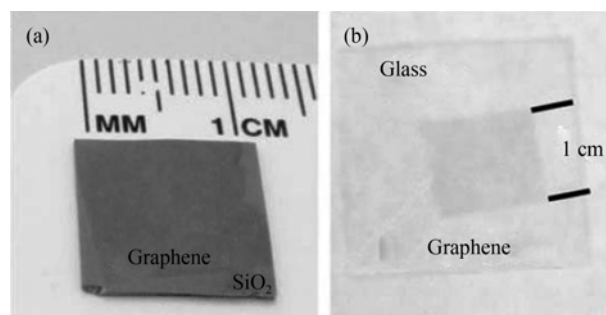


图 4 转移到  $\text{SiO}_2/\text{Si}$  基片(a)和玻璃板(b)上的石墨烯薄膜<sup>[61]</sup>

Fig. 4 Graphene films transferred onto a  $\text{SiO}_2/\text{Si}$  substrate (a) and glass plate (b)<sup>[61]</sup>

表 1 SiC 外延生长石墨烯概况  
Table 1 Epitaxial growth of graphene on SiC substrates

SiC Substrates	Fabrication of Graphene*	Characterization of Graphene	Ref.
Si-face 6H-SiC	CVD reactor, Ar atmosphere ((1500–1600)°C×90 min)	Thickness between 0.25 and 1 nm having a mobility of 860 cm <sup>2</sup> /(V·s) for an elec-tron concentration of 1.13×10 <sup>13</sup> cm <sup>2</sup>	[33]
C-face 6H-SiC	SiC sample covered with a graphite cap. RF heated furnace under high vacuum (1700°C×15 min)	Large, homogeneous, monolayer or bilayer graphene ribbons(600 μm long and 5 μm wide)	[34]
	AlN mask on the substrate. RF under high vacuum (~1.33×10 <sup>-4</sup> Pa) (1550°C×5 min)	A few layers graphene (FLG)	[35]
6H-SiC (0001)	Inductively heated furnace, 2000°C and at an ambient argon pressure of 1.013×10 <sup>5</sup> Pa.	Homogeneous large-area graphene layers	[36]
	UHV chamber (1.33×10 <sup>-8</sup> Pa), 1550°C	Bilayer graphene	[37]
Si-face 6H-SiC (0001)	Home-made MBE system equipped with RHEED (6×10 <sup>-8</sup> Pa) (1300°C×10 min)	About 4–10 layers graphene (by AFM)	[38]
C-face 6H-SiC (000 $\bar{1}$ )	UHV MBE chamber ((1030–1050°C)×(10–60) min)	Non-Bernal rotated graphene planes, single-layer or few layers graphene (FLG)	[39]
6H-SiC(0001) (mis-orientation within 0.03°)	2000°C and at an ambient argon pres- sure of 1 atm	Continuous graphene sheet, covering also the < 1.5 nm high steps, with a size larger than 50 μm <sup>2</sup>	[40]
6H-SiC(0001) (mis-orientation within 0.25°)	2000°C and at an ambient argon pres- sure of 1.013×10 <sup>5</sup> Pa	Continuous graphene, covering of also the 4.0–5.0 nm high steps, either in the form of long ribbons or large sheets	[40]
4H-SiC(0001)	LEEM instrument, 1300–1500°C	Bilayer and few layers graphene	[41]
Si-face 4H-SiC(0001)	Annealed (1450°C×2 min) under Ar flow(4.66×10 <sup>-2</sup> Pa) and then allowed to cool down in Ar	Two layer epitaxial graphene The RF-FETs with a peak cutoff frequency $f_T$ of 100 GHz for a gate length of 240 nm were fabricated using such graphene as the active layer	[42]
C-face 4H-SiC(000 $\bar{1}$ )	Heated for 10 min to temperatures $T > 1350^\circ\text{C}$ in vacuum	A mesh-like network of ridges with high curvature that bound atomically flat, tile-like facets of FLG	[43]
Si-face 4H-SiC	UHV(pressure <10 <sup>-6</sup> Pa) ((1200–1600)°C×(10–40)min)	Single layer or few layers graphene The Si-face graphene layers form after an interfacial layer is created	[44]
	CVD reactor under high vacuum condi- tions ((1225–1700)°C×(10–20)min)	Monolayer graphene (by Raman), a transitional layer between the substrate and the EG	[45]
C-face 4H-SiC	RF under high vacuum (<10 <sup>-4</sup> mbar) ((1400–1600)°C×(10–90)min)	Multilayer graphene without interfacial layer The presence of layers with carrier mobility greater than 250000 cm <sup>2</sup> /(V·s) (by FIR-MT)	[44]
	CVD reactor under high vacuum ((1225–1700)°C×(10–20)min)	Multilayer graphene forms directly on the C-face with- out transitional layer	[45]
3C-SiC(111)/Si(110)	UHV (1200°C×30 min)	Single- and two-layer graphene sheets	[46]
3C-SiC(111)/Si(111)	Resistively heated hot wall reactor ((1250–1350)°C×10 min)	Continuity on terraces and step edges suggesting the possibility of growing large scale graphene that could be suitable for future industrial applications	[47]

\* CVD: Chemical vapor deposition; UHV: Ultrahigh vacuum; RHEED: Reflection high-energy electron diffraction; RF: Radio frequency; AFM: Atomic force microscope; RF-FETs: Radio frequency field effect transistors; FIR-MT: Far-infrared magneto transmission; MBE: Molecular beam epitaxy

属表面中的 C 则在其表面重新析出结晶重构生长出石墨烯。

研究表明：在石墨烯生长过程中，当第一层石墨烯覆盖金属表面大约 80%时，第二层石墨烯才开始生长。底层石墨烯会与衬底产生强烈的相互作用<sup>[49]</sup>，而第二层与衬底之间只受到弱电耦合的作用，

可以与金属衬底完全分离，得到的单层石墨烯具有较好的电学性质。一旦当其表面被石墨烯完全覆盖后，石墨烯的生长立即停止，表现出自限制生长模式。因此，通过选择合适的金属衬底和工艺参数，即可实现大面积、高质量的石墨烯可控制备。但金属外延法制备的石墨烯的形貌和性能受金属衬底的

影响较大, 在晶格失配的过渡金属基底上, 石墨烯的起皱程度由界面处的化学键强度决定, 强化学键和晶格失配将导致石墨烯的高皱折度. 据文献报道, 金属和石墨烯界面处的轨道杂化程度为:  $\text{Pt}(111) < \text{Ir}(111) < \text{Rh}(111) < \text{Ru}(001)^{[50]}$ . 典型的金属衬底外延生长石墨烯的研究概况如表 2 所示.

3 石墨烯器件应用

3.1 超级电容器

超级电容器是一个高效储存和传递能量的体系, 它具有功率密度大、容量大、使用寿命长、经济环保等优点, 广泛应用于各种能源领域. 石墨烯具有理论比表面积高达  $2630\text{m}^2/\text{g}$ 、优异的导电性能和稳定性等, 作为电容器材料具有比单壁和多壁碳纳米

管更优异的性质, 使其有望成为超级电容器的理想电极材料<sup>[69]</sup>, 其性能与石墨烯的质量、层数和比表面积直接相关. Wang 等<sup>[70]</sup>通过肼还原氧化石墨烯得到的石墨烯在含水电解质溶液中的比电容可高达  $205\text{F/g}$ , 经过 1200 次的试验后其比电容还仍达到原来的 90%, 其石墨烯电容器如图 5 所示. 吴忠帅等<sup>[71]</sup>采用溶胶-凝胶法和低温处理方法设计合成了一种水合氧化钨/石墨烯复合超级电容器电极材料, 研究表明具有较高的比容量( $570\text{F/g}$ )和优异循环稳定性(1000 次循环后容量保持率为 97.9%). 石墨烯表面可以形成双电层, 有利于电解液的扩散, 因此基于石墨烯的超级电容器具有良好的功率特性, 其最近的研究进展如表 3 所示.

3.2 场效应晶体管

在石墨烯众多的电子器件应用当中, 场效应晶

表 2 不同金属衬底外延生长制备石墨烯的研究概况  
Table 2 Epitaxial growth of graphene on metal substrates

Metal Substrates	Carbon sources	Characterization of Graphene	Ref.
Ru(0001)	C <sub>2</sub> H <sub>4</sub>	Highly ordered, millimeter-scale, continuous, single-crystalline graphene monolayer stabilizing at high temperatures	[51]
Ru(0001)/sapphire (0001)	C <sub>2</sub> H <sub>4</sub>	High-quality graphene with uniform monolayer thickness and full surface coverage	[52]
Ir(111)	C <sub>2</sub> H <sub>4</sub>	Continuous, low defect and micron-scale monolayer graphene	[53-54]
Ni films (300nm thickness)	CH <sub>4</sub>	Large area (cm <sup>2</sup> ) films of single- to few-layer graphene, Single- or bilayer regions can be up to 20 $\mu\text{m}$ in lateral size	[55]
Ni layer (>300nm thickness)	CH <sub>4</sub>	Large-scale graphene films transferring them to arbitrary substrates, The transferred graphene films show very low sheet resistance of 280 $\Omega$ per square, with 80% optical transparency	[56]
Ni nanowire templates	C <sub>2</sub> H <sub>4</sub>	Large-diameter graphene nanotubes with shells comprising a few or many layers, Number of graphene layers grown for different ethylene feeding times	[57]
Ni(111)	C <sub>3</sub> H <sub>6</sub>	An ordered passivated graphene layer, The spin-polarization of the secondary electrons obtained from this system upon photoemission does not change upon large oxygen exposure	[58]
Ni particles	CH <sub>4</sub>	Bulk growth of mono- to few-layer graphene	[59]
Cu or Ni	Graphite	Bulk graphite films and growth of large-area single layer or few-layer graphene	[60]
Cu foils (20 $\mu\text{m}$ thickness)	CH <sub>4</sub>	Large-area, high-quality and uniform graphene films of the order of centimeters (Fig. 4)	[61]
Cu foils (25 $\mu\text{m}$ thickness)	CH <sub>4</sub>	Large single-crystal graphene, hexagonally-shaped grains (with sizes of tens of microns) have their edges macroscopically oriented predominantly parallel to zig-zag directions	[62]
Cu(111)	C <sub>2</sub> H <sub>4</sub>	Numerous domain boundaries with increasing coverage	[63]
		Reducing the density of domain boundaries is one challenge of growing high-quality graphene on copper	
		Large-area monolayer graphene	
		The film quality is limited by grain boundaries, and the best growth is obtained on this surface than other surface of Cu	[64]
Rh(111)	C <sub>3</sub> H <sub>6</sub>	Monolayer graphite (MG)	[50]
Pt(111)	CH <sub>4</sub>	Highly oriented and chemically inert MG without unidentified carbon-related residues	[65]
Co(0001)	C <sub>3</sub> H <sub>6</sub>	Continuous multilayer graphene, the high spin polarization of secondary electrons is confirmed for graphene/Co(0001) with higher values (25%) due to the larger magnetic moment of Co	[66]
Co films /sapphire	CH <sub>4</sub>	Uniform and orientation-controlled single-layer graphene over the Co film	[67]
Stainless steel	Aliphatic alcohols	Single- to multi-layer graphene that growth occurs on FeO rich regions	[68]

表 3 石墨烯在超级电容器中的应用概况

Table 3 Applications and Properties of graphene based supercapacitor devices

Electrode Materials	Electrolytes*	Characterization of Graphene	Ref.
Graphene prepared by exfoliation of GO	H <sub>2</sub> SO <sub>4</sub>	Specific capacitance: 117 F/g (operating voltage: 3.5 V)	[72]
	PYR <sub>14</sub> TFSI	Specific capacitance: 75 F/g (operating voltage: 3.5 V)	[72]
		Energy density: 31.9 Wh/kg	
Chemically modified graphene (CMG)	KOH	Specific capacitance: 135 F/g (operating voltage: 1 V)	[73]
	TEABF <sub>4</sub> /AN	Specific capacitance: 99 F/g (operating voltage: 2.5 V)	[73]
Graphene materials (GMs) prepared from graphene oxide sheets	KOH	Specific capacitance: 205 F/g, Power density: 10 kW/kg, Energy density: 28.5 Wh/kg	[70]
		Retained ~90% specific capacitance after 1200 cycle tests	
RuO <sub>2</sub> /graphene composite	NaOH	Specific capacitance: 570 F/g, Power density: 10 kW/kg, Energy density: 20.1 Wh/kg	[71]
		Retained ~97.9% specific capacitance after 1000 cycle tests	
Graphene nanosheet/carbon black composites (9:1)	KOH	Specific capacitance: 175.0 F/g at 10mV/s, 118.1 F/g at 500 mV/s Retained ~90.9% specific capacitance after 6000 cycle tests	[74]
Graphene-PANI	H <sub>2</sub> SO <sub>4</sub>	Specific capacitance: 300–500 F/g at a current density of 0.1 A/g	[75]
Graphene nanosheet/carbon nanotube/polyaniline (GNS/CNT/PANI)	KOH	Specific capacitance: 1035 F/g at 1mV/s	[76]
		Retained ~94% specific capacitance after 1000 cycle tests	
Graphene-MnO <sub>2</sub> composite (78wt% MnO <sub>2</sub> )	Na <sub>2</sub> SO <sub>4</sub>	Specific capacitance: 310 F/g at 2 mV/s, 228 F/g at 500 mV/s	[77]
		Retained ~95.4% specific capacitance after 15000 cycle tests	
Graphene prepared by MWI reduced GO	H <sub>2</sub> SO <sub>4</sub>	Specific capacitance: 147.5 F/g at 10 mA/cm <sup>2</sup>	[78]

\* PYR<sub>14</sub>TFSI: N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide; TEABF<sub>4</sub>: tetraethylammonium tetrafluoroborate; MWI: micro-wave irradiation; AN: acetonitrile; GO: graphite oxide; PANI: polyaniline

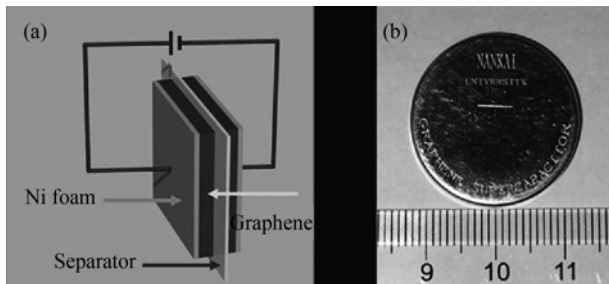


图 5 (a)石墨烯超级电容器装置原理图, (b)产业级硬币状的石墨烯超级电容器光学图片<sup>[70]</sup>

Fig. 5 (a) Schematic diagram of a graphene-based supercapacitor device, (b) An optical image of an industry-grade coin-shaped graphene-based supercapacitor device<sup>[70]</sup>

晶体管(Field-Effect Transistors: FET)是其代表之一<sup>[1]</sup>. 制作体积更小, 频率更高, 运算速度更快的晶体管是当前微电子研究领域的热点和重点, 也是进一步延续摩尔定律的重要保证. 石墨烯因其超薄结构以及优异的物理特性, 在 FET 应用上展现出了优异的性能和诱人的应用前景. 如 Obradovic 等研究发现, 与碳纳米管相比, 石墨烯 FET 拥有更低的工作电压<sup>[79]</sup>; Wang 等所制备的栅宽 10nm 以下的石墨烯带 FET 的开关比达 10<sup>7</sup><sup>[80]</sup>; Wu 等<sup>[81]</sup>采用热蒸发 4H-SiC 外延生长的石墨烯制备的 FET, 其电子和空

穴迁移率分别为 5400 和 4400 cm<sup>2</sup>/(V·s), 比传统半导体材料如 SiC 和 Si 高很多; Lin 等<sup>[82]</sup>制备出栅长为 350nm 的高性能石墨烯 FET, 其载流子迁移率为 2700cm<sup>2</sup>/(V·s), 截止频率为 50GHz, 并在后续研究中进一步提高到 100GHz<sup>[83]</sup>(图 6); Liao 等<sup>[84]</sup>所制备的石墨烯 FET 的跨导达 3.2mS/μm, 并获得了迄今为止最高的截止频率 300GHz<sup>[85]</sup>, 远远超过了相同栅长的 Si-FET(~40GHz).

然而, 由于石墨烯的本征能隙为零, 并且在费米能级处其电导率不会像一般半导体一样降为零, 而是达到一个最小值, 这对于制造晶体管是致命的, 因为石墨烯始终处于“开”的状态. 另外, 带隙为零意味着无法制作逻辑电路, 这成为石墨烯应用于晶体管等器件中的主要困难和挑战. 因此, 如何实现石墨烯能带的开启与调控, 亟待研究和解决. 据文献报道, 一般采用两种方法实现石墨烯能带的开启与调控, 即: 掺杂改性<sup>[86]</sup>和形貌调控<sup>[87]</sup>. *Nature Nanotechnology* 评论明确指出<sup>[88]</sup>: 要深入挖掘石墨烯的优异物理特性, 以制备高性能石墨烯 FET, 其重要基础和关键之一是获得宽度与厚度(即层数)可控的高质量石墨烯带状结构. 带状石墨烯因其固有而独特的狭长“扶椅”或“之”状边缘结构效应、量子限域效应而具有丰富的能带结构<sup>[89]</sup>, 其能隙随着石

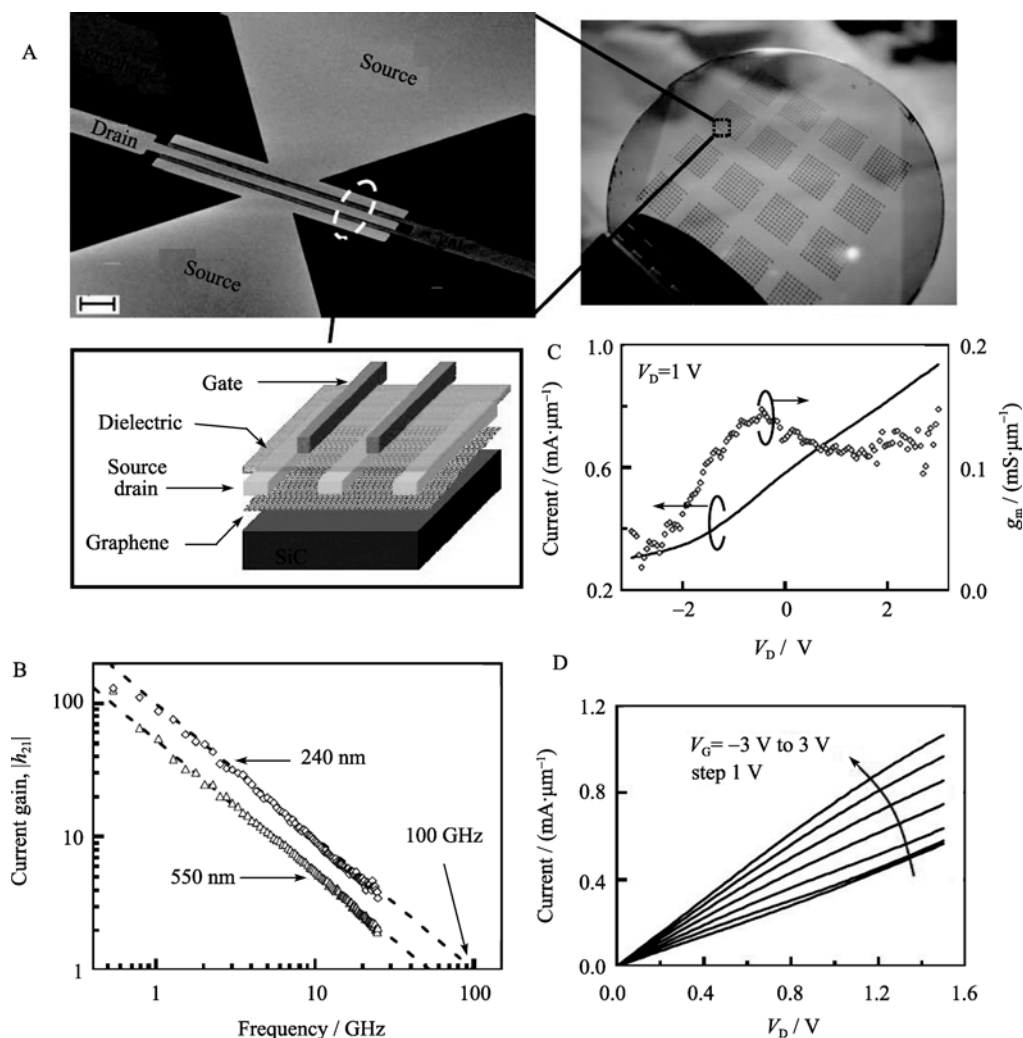
图 6 石墨烯 FET<sup>[83]</sup>

Fig. 6 Graphene field-effect transistors

(A) SEM image and the schematic cross-sectional view of a top-gated graphene FET, (B) Measured small-signal current gain as a function of frequency for graphene FET, (C) The drain current of graphene transistor as a function of Gate voltage and (D) The measured drain current as a function of drain bias of a graphene FET<sup>[83]</sup>

石墨烯的宽度减小而增大<sup>[90]</sup>, 且和石墨烯的厚度密切相关<sup>[91]</sup>, 成为石墨烯 FET 沟道材料的理想选择. 据文献报道, 最具代表性的制备石墨烯带的方法有: 化学气相沉积法<sup>[92]</sup>、纳米结构模板法<sup>[93]</sup>、化学腐蚀多壁碳纳米管法<sup>[94]</sup>、等离子体刻蚀多壁碳纳米管法<sup>[95]</sup>等. 然而, 上述方法难以实现石墨烯带状结构的精细控制. 以腐蚀与刻蚀碳纳米管为例, 最终获得的石墨烯带实际上依赖于原碳纳米管的直径, 且其带状结构的产率有待提高. 如何实现石墨烯带高质量大面积生长及其宽度和厚度控制, 是当前面临的困难和挑战.

### 3.3 发光二极管的电极材料

氧化铟锡(ITO)作为传统电极, 广泛应用于太阳能电池、发光二极管(LED)和有机发光二极管(OLED)等领域. 由于铟元素在地球上的含量有限,

价格昂贵, 特别是其毒性大, 使其应用受到限制. 另外, ITO 在蓝光、紫外和近红外光范围内的透明度较差, 在酸或强碱中不稳定, 离子容易扩散到基底等缺点, 因此研发一种可取代 ITO 的电极材料显得尤为重要.

石墨烯具有高透明度(几乎完全透明, 只吸收不到 2.3% 的太阳光<sup>[96]</sup>)和优异电学性能, 使其有可能成为 ITO 的理想替代材料. Kim 等<sup>[56]</sup>的研究证明其还是制作柔性透明电极的理想材料: 他们通过用化学气相沉积法(CVD)在 300nm 的 Ni 薄膜上生长石墨烯, 并将其成功转移到其它衬底, 其透光率达 80%. 如果进一步减少生长时间和 Ni 层厚度, 石墨烯的透明度有望提高到 93%. Jo 等<sup>[97]</sup>用 CVD 法在 Ni 薄层上生长多层石墨烯(MLG), 其电阻约为 620 $\Omega$ , 在 400~600nm 波长范围内的透明度高于 85%.

Wu 等<sup>[98]</sup>将 MLG 用作氮化镓(GaN)基蓝光 LEDs 的透明导电电极(如图 7 所示), 并与 GaN 基 LEDs 的传统电极 ITO 做了比较: 在输入电流小于 10mA 时, MLG 为电极与 ITO 为电极的 GaN 基 LEDs 的输出功率相当; 在输入电流大于 10mA 时, 相比 ITO, MLG 可降低电极接触电阻和表面电阻. 通过进一步优化石墨烯的质量和厚度, 有望进一步提高发光二极管的性能, 其核心问题是如何将高质量的石墨烯转移到低成本的塑料基底上. Kim 等<sup>[99]</sup>首次将石墨烯应用于 GaN 紫外发光二极管(UV-LED)的透明导电电极. 石墨烯基透明导电电极相对于 ITO(11~12 W/m<sup>2</sup>·K)和标准的 Ni/Au 金属化电极来说, 具有高导热系数(~5000W/(m·K))和较好的紫外传递能力.

### 3.4 锂离子电池正极材料

锂离子电池的能量密度和性能主要取决于阴阳极材料的物理化学特性. 商业锂离子电池的阳极材料主要是石墨, 但由于其理论比容量低(只有 372mAh/g), 无法满足便携式电子设备和电动车的需求. 石墨烯被发现后, 立即引起了锂离子电池研究领域的关注.

石墨烯在锂离子的存储方面表现出优异的电化学性能. 相对于石墨而言, Yoo 等<sup>[100]</sup>研究发现, 石墨烯的比电容(540 mAh/g)更高, 当在石墨烯纳米片中掺入大分子的 CNTs 和 C<sub>60</sub> 后, 其比电容分别提高到 730 和 784mAh/g. Lian 等<sup>[101]</sup>的研究表明, 以石墨烯为阳极材料的锂离子电池具有更加优异的性能(如图 8 所示): 在电流密度为 100mA/g 时, 其可逆比电容高达 1264mAh/g; 在循环使用 40 次后, 可逆比电容仍保持在 848mAh/g; 甚至在电流密度高达 500mA/g 时, 其可逆比电容仍然可达到 718mAh/g. 石墨烯的高可逆容量, 高循环性能和高充放电速率等优异特性, 使得石墨烯有望成为电池阳极材料的优异候选材料之一.

## 4 结束语

近几年, 石墨烯在微电子、量子物理、材料、化学等领域都表现出许多独特而优异的性能和潜在的应用前景, 在超级电容器、场效应晶体管、发光二极管、锂离子电池等器件应用方面取得了较好的

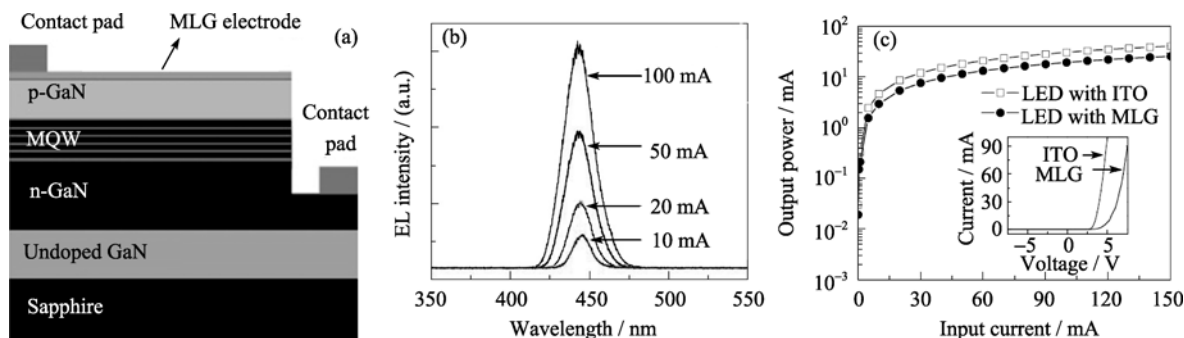


图 7 透明石墨烯为电极的 GaN 基 LEDs<sup>[97]</sup>

Fig. 7 The GaN-based LED structure with a transparent MLG electrode<sup>[97]</sup>

(a) Schematic cross-sectional view of the GaN-based LED structure with a transparent MLG electrode, (b) EL spectra of a GaN LED with transparent MLG electrodes at input currents of 10, 20, 50, and 100 Ma, (c) Light output powers of a GaN LED with MLG electrodes and ITO electrodes as a function of input current

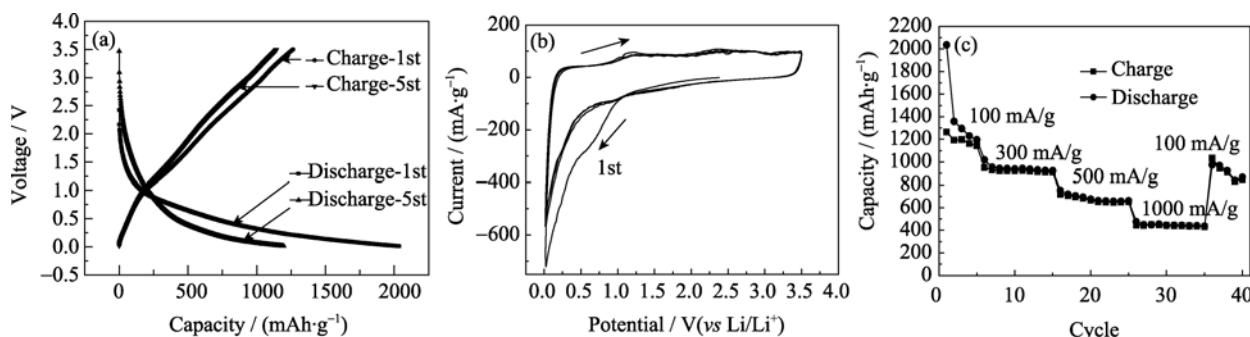


图 8 石墨烯为正极材料的锂离子电池特性<sup>[101]</sup>

Fig. 8 The properties of graphene sheets as an anode material for lithium-ion batteries<sup>[101]</sup>

(a) First and fifth discharge/charge profiles of graphene sheets at the current density of 100mA/g, (b) Cyclic voltammograms (CV) of graphene sheets, (c) Cycle performance of graphene sheets at the current densities from 100 mA/g to 1000 mA/g



研究成果和进展. 迄今为止, 石墨烯研究和应用的重点和难点之一依然是其大规模、低成本、可控生长和制备. 在众多的石墨烯制备方法中, 外延生长法有望成为高质量、与传统电子工艺兼容、低成本、大面积的宏量制备技术, 已经初步实现了从纳米、微米、厘米石墨烯的成功制备, 同时可实现石墨烯从单层、双层到少数层的调控. 相信在众多科研工作者的不断努力之下, 石墨烯改变人们的生活将不再遥远.

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