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专题：二维材料与器件(Ⅰ) 评 述

绝缘衬底上石墨烯的化学气相沉积制备与器件应用

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摘要 石墨烯作为一种拥有优异性能的二维晶体材料，其制备方法与潜在应用在最近几年内得到了广泛研究．与现有半导体硅工艺相匹配的化学气相沉积方法因其能够以低成本大规模制备高质量石墨烯，逐渐成为工业化大规模制备石墨烯的首选技术．然而，金属上通过化学气相沉积生长的石墨烯需要转移到绝缘衬底上才可以用于器件制备、电学性能表征等后期工作，而目前的转移技术无法避免对石墨烯的质量造成影响．如果在绝缘衬底表面直接生长石墨烯将有效避免石墨烯的转移工艺，从而有望在目标绝缘衬底上直接获得大面积高质量石墨烯．本文系统性介绍了近几年来绝缘衬底上生长石墨烯的相关研究进展，总结并展望了绝缘衬底上石墨烯生长、应用的发展前景与需要攻克的难题．

关键词 石墨烯，化学气相沉积，绝缘衬底，金属衬底，氮化硼

石墨烯是一种由碳原子通过sp^{2}轨道杂化构成的六角蜂窝结构，且只有单原子层厚度的二维晶体材料，拥有优异的物理、化学性质，如室温下亚微米载流子平均自由程、高达200000 cm^2 V^{-1} s^{-1}的载流子迁移率、分数量子霍尔效应、高透光率和机械强度等[1~4]．因此，自2004年首先被Geim研究组[5]分离以来就受到了广泛的关注和研究．石墨烯不仅为许多新奇的应用带来了可能[6,7]，而且被国际半导体技术路线图列为有望延续摩尔定律的新材料，将广泛应用于新型纳米电子器件和高性能集成电路中．以石墨烯为代表的二维晶体材料在替代传统半导体材料走向微纳电子领域，应用于大规模集成电路制造中充满了机遇，同时也面临许多亟需解决的重大科学难题．为了充分利用石墨烯的优异性能，大规模高质量石墨烯的可控制备是需要解决的首要难题．

在众多石墨烯制备方法中[8~13]，化学气相沉积法(CVD)在制备高质量、大尺寸石墨烯方面显示出巨大的优势[11~13]，该方法成本低廉，更能够和目前的集成电路工艺相兼容．随着技术的不断进步，采用CVD方法已经可以制备出尺寸达30英寸(1英寸=2.54 cm)的石墨烯连续薄膜[13]，为石墨烯在电子器件中的广泛应用奠定了良好的基础．近年来，金属上通过CVD法生长石墨烯的生长机理已经得到了充分研究并被认同，其主要分为两种：(1) 相对溶碳能力较弱的金属(如Cu，Ge等)，主要生长机理为金属的表面催化机制[14,15]；(2) 相对有较高溶碳能力的金属(如Ni, Ru等)，主要生长机理为碳的溶解析出机制[14,16,17]．得益于对生长机理的充分理解，最近，金属上CVD法制备石墨烯已经取得了许多重大突破．Wu等人[11]成功在Cu-Ni二元合金上通过局域供碳的方法，制备出了晶圆级石墨烯大单晶，且证明了其具有较高的电学性能．Xu等人[12]利用氧气辅助方法，成功在Cu

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上实现了大尺寸石墨烯的超快生长. 这些重大突破将显著促进石墨烯的工业化大规模应用.

然而, 金属上CVD制备的石墨烯必须转移到绝缘衬底上才能进行器件制备、性能表征等后期工作, 复杂的转移过程将不可避免地给石墨烯的晶体质量和物理性能造成影响. 近年来, 多种改进的石墨烯转移方法被提出并得到了有效应用, 这些方法显著降低了石墨烯转移过程中的褶皱和破损等问题[18~20]. 但是转移过程耗时长、污染环境且费用高昂的难题仍然没有得到有效解决. 在绝缘衬底上直接生长石墨烯能避免后续转移过程, 有望在目标衬底上直接获得高质量石墨烯并提高相应石墨烯器件的性能, 扩展石墨烯的应用范围, 这对石墨烯的进一步应用和研究有重大意义.

近年来, 绝缘衬底上生长石墨烯得到了大量研究[21~33], 研究者提出许多新策略和实验方案用于包括在h-BN[29], SiO_2/Si[31], 石英[30]、蓝宝石(Al_2O_3)[28]、$SrTiO_3$[32]乃至普通玻璃[33]等不同绝缘衬底上直接生长石墨烯. 然而, 与金属上CVD法生长石墨烯不同, 绝缘衬底由于没有来自衬底的催化作用且基本不溶碳, 缺乏使碳源裂解、成核及生长的驱动力. 因此绝缘衬底上的石墨烯生长常会遇到成核密度高、生长速度慢、晶畴尺寸小、晶格缺陷多、电学性能差等问题. 到目前为止, 虽然有大量的研究绝缘衬底上石墨烯的形核与生长机理的工作, 但是尚没有实现绝缘衬底上生长大面积高质量石墨烯, 此领域仍需要更深入的研究. 本文将以生长机理为分类, 介绍目前为止发展出来的多种绝缘衬底上生长石墨烯及器件应用的相关技术, 并展望了其发展前景及需要攻克的难题.

1 无催化辅助直接生长石墨烯

无催化辅助直接生长石墨烯, 即在绝缘衬底上不外加辅助条件直接生长石墨烯. 相对于金属衬底上CVD生长的石墨烯, 这种方法有助于省去石墨烯转移这一步骤, 显著改善石墨烯破损、褶皱、界面沾污等问题. 目前, 已有大量的针对无催化辅助直接生长石墨烯的相关研究报道. 北京大学刘忠范研究组[30,32~35]在多种绝缘衬底上直接生长石墨烯领域开展了系列工作. 他们在软化温度约600℃的普通玻璃上成功生长出了高质量石墨烯[33], 这项工作极大促进了石墨烯玻璃的规模化生长, 有助于石墨烯在显示屏等领域的应用(图1(a), (b)). 最近, 他们利用乙醇作为碳源, 成功制备了25英寸的石墨烯玻璃[35](图1(c), (d)), 该工作将有助于石墨烯玻璃在工业领域的应用. 除了玻璃衬底, 他们也成功实现了高介电常数衬底如$SrTiO_3$上的石墨烯直接生长[32]. 与低介电常数衬底(如SiO_2)相比, $SrTiO_3$能够有效减少栅极漏电、提升栅极电容从而获得更佳的栅极调制效果(图1(e)~(g)).

除了玻璃和$SrTiO_3$衬底, 研究人员也成功在包括SiO_2/Si, Si_3N_4在内的多种绝缘衬底上直接生长石墨烯. 中国科学院化学研究所刘云圻研究组[25]利用近平衡法, 在SiO_2/Si, Si_3N_4, 石英、蓝宝石等多种绝缘衬底上成功直接生长石墨烯. 其中, SiO_2/Si上生长的石墨烯能很好地和现有半导体硅工艺相结合, 且能直接制备多种器件并进行电学性能表征. 刘云圻研究组[31]还利用预先处理的SiO_2/Si衬底成功制备出了较高质量的石墨烯(图2(a)~(c)). 通过分别在空气和H_2中对衬底进行预处理, 他们发现氧能有效提高石墨烯的形核密度. 理论计算表明, 衬底表面处的氧能提高C–C键结合的几率, 促进石墨烯的生长. 除了预先对衬底进行处理, 调节CVD过程中的生长参数也能成功地在绝缘衬底上直接生长较高质量的石墨烯, 刘云圻研究组[24]利用两段法成功在Si_3N_4上制备出了高质量石墨烯. 为了避免形核过程和生长过程的竞争, 通过使用较低浓度的甲烷来降低形核密度, 形核阶段过后, 提高甲烷浓度以促进石墨烯的生长(图2(d)~(f)). 此外, 通过调节形核和生长过程中的反应温度也能实现同样的效果, Hwang等人[36]利用此方法成功在蓝宝石衬底上直接制备了较高质量的石墨烯.

h-BN作为一种新型衬底, 由于其具有良好的绝缘性、原子级平整的台面、没有悬挂键以及晶格常数与石墨烯接近, 用h-BN作为石墨烯的衬底能最大限度地保留石墨烯的本征特性, 且用其制备的石墨烯器件表现出优于其他衬底(如SiO_2/Si)的电学性能, 因此近几年h-BN上生长石墨烯被广泛研究[29,37~40]. 本研究组[29,38,41]在剥离h-BN上生长石墨烯领域开展了一系列工作. 以硅烷/氩气混合气体做载气, 以乙炔为源气, 可以显著提升h-BN上石墨烯的生长速度. 如图2(g)~(i)所示, 通过引入硅烷和锗烷等气体, 石墨烯的生长速率提高了超过2个数量级, 在h-BN表面获得了直径达到20 μm的高质量石墨烯单晶. 此外, 通过观察石墨烯在氮化硼表面取向外延产生的摩尔条纹, 结果发现石墨烯晶格可以很好地与h-BN晶格匹配, 且在来自不同形核中心的石墨烯晶体边界融合处没有发现晶界, 这极大提升了h-BN上石墨烯的

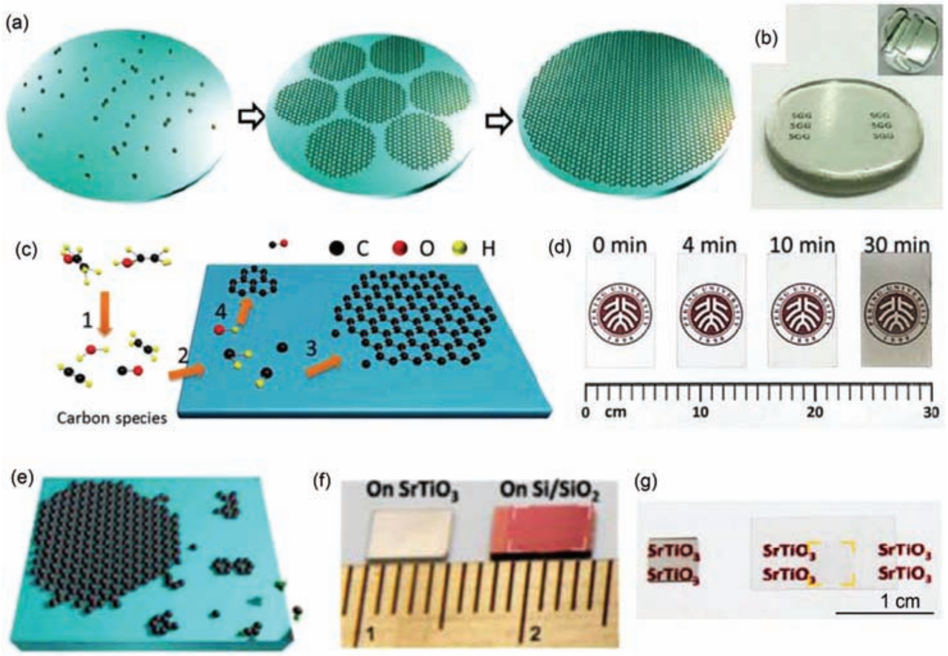

图 1 石墨烯在熔融态玻璃、耐高温玻璃、高介电常数衬底上免转移直接生长示意图与典型结果. (a) 石墨烯在熔融玻璃上生长过程示意图. (b) 石墨烯玻璃板照片. (c) 利用乙醇作为碳源在固态石英玻璃上低压生长石墨烯过程示意图. (d) 10 cm×6 cm石墨烯玻璃样品照片. (e) 石墨烯在钛酸锶(STO)衬底上生长示意图. (f) 钛酸锶衬底和转移到Si/SiO$_2$(厚度 300 nm)衬底上的石墨烯照片. (g) 钛酸锶石墨烯样品(左)和转移到PET薄膜(右)上的石墨烯样品照片

Figure 1 Schematic and typical results of graphene growth on molten glass, high-temperature-resistance glass and high-kappa dielectric substrates. (a) Schematic of graphene growth on molten glass. (b) Photograph of an as-grown graphene glass plate. (c) Schematic of graphene growth on solid quartz glass by the LPCVD method using ethanol as precursor. (d) Photographs of as-grown graphene-glass samples (10 cm×6 cm). (e) Schematic of graphene growth on SrTiO$_3$ substrates. (f) Photograph of an as-grown graphene film on STO and a transferred graphene film to Si/SiO$_2$ (300 nm thickness) substrate. (g) Photograph of an as-grown graphene/STO sample (left) and a transferred graphene film to a PET sheet (right)

性能，为制备高性能的h-BN/石墨烯器件带来了可能.

2 等离子体辅助低温生长石墨烯

如前所述，由于没有催化活性，常见碳源分子如CH$_4$比较难在绝缘衬底表面裂解成CH$_x$以及游离碳，而且游离碳在绝缘衬底上的迁移比较困难，因此在绝缘衬底上直接生长石墨烯一般需要较高的生长温度和较长的生长时间. 曾在制备碳纳米管过程中广泛使用的等离子增强化学气相沉积法(PECVD)[42,43]，是一种可以借鉴的方法. 等离子体由于具有较高的能量和较强的化学活性，在CVD过程中能显著降低碳源分子的裂解反应温度，从而促进石墨烯的形核和生长.

2008年, Dato等人[44]最早使用等离子体制备石墨烯. 他们利用Ar等离子体辅助和液态乙醇为碳源，成功制备出了无需衬底的单层和双层石墨烯薄膜，给PECVD制备石墨烯提供了新思路. 2009年, Yuan等人[45]首次成功利用微波等离子体制备了高质量、高产率石墨烯薄膜，他们利用甲烷/氢气混合气(体积比1∶9)，在30 Torr(1 Torr≈133.322 Pa)和200 sccm(sccm, 每分钟标准立方厘米)的流量下，在不锈钢衬底上制备出了1~3层的石墨烯，并且发现石墨烯具有较高的纯度，没有生成碳纳米管. 随后的2011年，Zhang等人[46]成功利用PECVD实现了石墨烯在绝缘衬底上的范德瓦尔斯外延生长(图3(a)~(d)). 他们发现利用远程-PECVD)(remote-PECVD，r-PECVD可以在低至550℃的生长温度下，在多种绝缘衬底上成功生长高质量石墨烯薄膜. 此后，Zhang研究组[47]通过低温PECVD技术在h-BN表面制备得到了较高质量的石墨烯(图3(e)~(g))，电学测试结果表明其内部载流子迁移率达到了4000 cm^2 V^{-1} s^{-1}. 为了进一步提高PECVD生长石墨烯的质量，Wei等人[48]利用“临界”-PECVD)(critical-PECVD，c-PECVD成功在包括SiO$_2$/Si、蓝宝石等衬底上制备出了微米级六角石墨烯单晶，显著提高了PECVD生长石墨烯的质量. 他们以H$_2$作为等离子体，刻蚀石墨烯生长过程中的缺陷以及使石墨烯边界活性化，让石墨烯的刻蚀和生长过程达到一

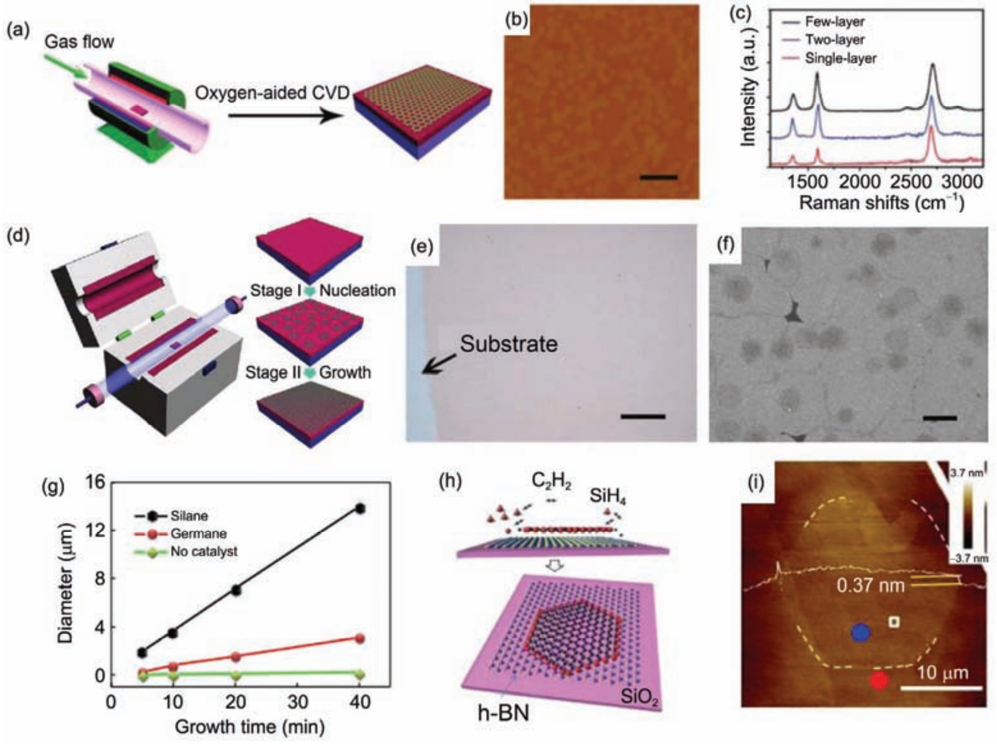

图 2 氧辅助、两段法、硅烷催化直接生长石墨烯示意图与典型结果. (a) SiO_2/Si衬底上氧辅助CVD生长石墨烯示意图. (b) 石墨烯薄膜的原子力显微镜(AFM)相图. (c) 石墨烯薄膜的拉曼光谱(激光波长 514 nm). (d) Si_3N_4上石墨烯生长的CVD系统与两段法生长石墨烯工艺示意图. (e) Si_3N_4上石墨烯薄膜的光镜图, 标尺为 50 μm. (f) 石墨烯薄膜的扫描电子显微镜(SEM)图, 标尺为 500 nm. (g) 不同催化剂条件下石墨烯单晶尺寸与生长时间关系图. (h) 气态催化剂辅助CVD生长工艺示意图. (i) 典型的 20 μm石墨烯单晶的表面形貌图, 点画线表示了石墨烯晶核的轮廓

Figure 2 Schematic and typical results of oxygen-aided, two-stage method and silane-catalyzed direct synthesis of graphene. (a) Schematic diagram of the oxygen-aided CVD growth of graphene on a SiO_2/Si substrate. (b) AFM phase image of graphene sheets. (c) Raman spectra (laser wavelength 514 nm) of a graphene film. (d) CVD system for graphene growth on a Si_3N_4 substrate and the schematic diagram of the two-stage process for graphene growth. (e) Optical micrograph of a graphene film on a Si_3N_4 substrate. Scale bar: 50 μm. (f) SEM image of graphene film. Scale bar: 500 nm. (g) The growth duration dependence of the domain dimensions for single-crystalline graphene in the presence of silane or germane gaseous catalysts and no catalyst. (h) Schematic of the gaseous catalyst-assisted chemical vapor deposition process. (i) Topography image of a typical single-crystalline graphene domain with a diameter of 20 μm. The dashed line frames the shape of the graphene grain

个严格的平衡状态, 从而实现了高质量石墨烯单晶的生长(图3(h)~(j)). 随后, Wei等人[49]又引入NH_3作为N源, 通过调节平衡生长温度和NH_3含量的关系, 在低至435℃的生长温度下, 成功实现了生长N掺杂石墨烯, 此工作显著提高了N掺杂石墨烯的质量. 但是, 目前该方法还存在一些问题, 采用PECVD低温制备的石墨烯生长速度仍然较慢且难以制备大面积石墨烯连续薄膜, 在控制石墨烯层数、抑制碳的三维生长等方面也面临一定的困难.

3 绝缘衬底-金属覆盖层界面处生长石墨烯

受启发于金属衬底表面CVD生长高质量石墨烯, 研究人员通过结合金属覆盖层(如Cu, Ni等)和绝缘衬底, 成功实现了在绝缘衬底-金属覆盖层界面处生长高质量石墨烯[21,23,26,50~52]. 该方法的另一个好处就是可以通过对金属覆盖层的图形化实现对石墨烯的图形化, 从而满足特殊器件应用的需求. 绝缘衬底-金属覆盖层界面处生长石墨烯的一般模式有两种: 一种为绝缘衬底-含碳层-金属覆盖层, 该模式下, 含碳层在金属覆盖层的催化下直接生长于绝缘衬底-金属覆盖层界面处[21,22]; 另一种为绝缘衬底-金属覆盖层-含碳层, 该模式下, 碳原子在CVD过程中穿过金属层渗透到绝缘衬底-金属覆盖层界面处并形核长大[23,26].

目前, 在绝缘衬底-金属覆盖层界面处生长石墨烯已经取得了大量进展. Levendorf等人[53]首次成功实现了利用Cu膜催化碳源的分解, 直接在绝缘衬底上生长大尺寸单层石墨烯, 并实现了高质量晶体管

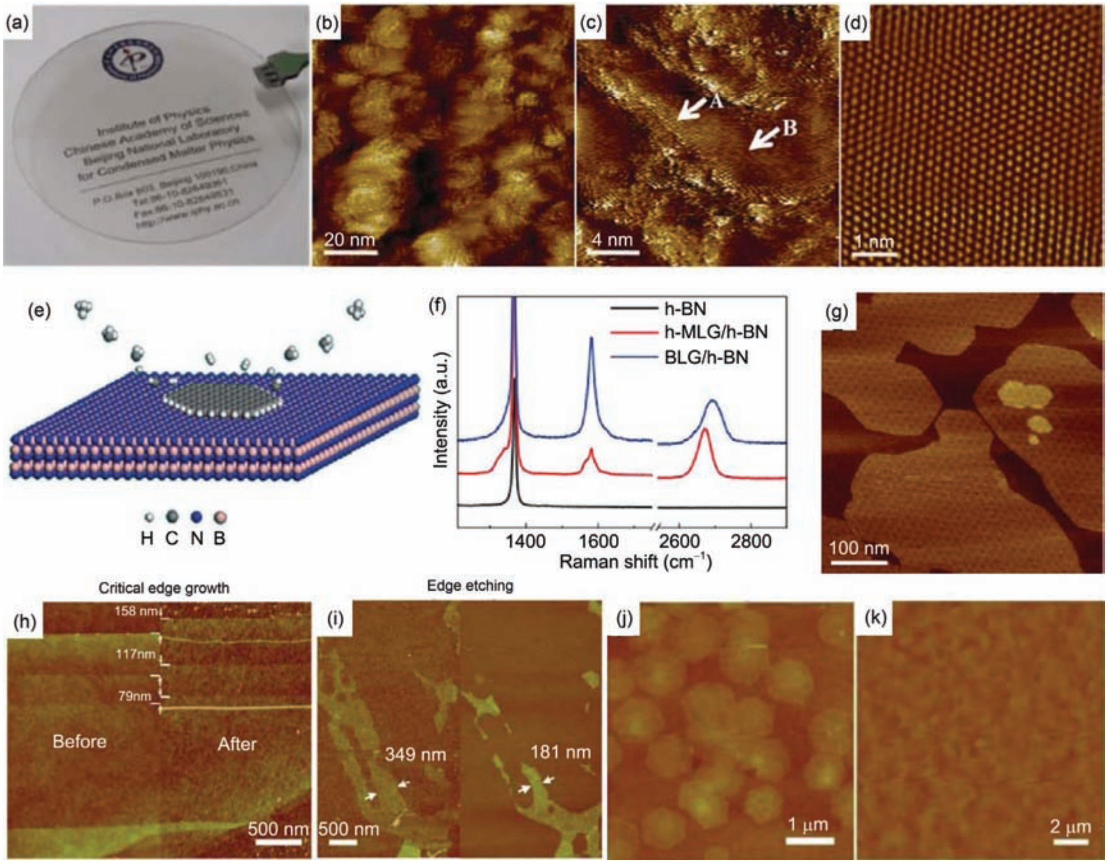

图 3 等离子体辅助在多种绝缘衬底上免转移生长石墨烯. (a) 4英寸晶圆级纳米石墨烯薄膜照片. (b)~(d) SiO_2衬底上纳米石墨烯扫描隧道显微镜(STM)图. (b) 高度图; (c) (b)的放大图; (d) 对区域B进行傅里叶变换后. (e) 生长机制示意图. (f) 六角单层石墨烯晶核(h-MLG), 双层石墨烯薄膜(BLG)和纯六方氮化硼(h-BN)衬底的拉曼光谱. (g) 晶核的摩尔条纹. (h) 剥离石墨烯在PECVD前后的AFM图. (i) 剥离石墨烯片被处理后的AFM图. (j) SiO_2/Si上HGCs经过c-PECVD生长后的AFM图. (k) SiO_2/Si上石墨烯膜的AFM图

Figure 3 Plasma-assisted direct synthesis of transfer-free graphene on various dielectric substrates. (a) Optical image of a 4-inch wafer scale nano-graphene film. (b)–(d) STM images of the nano-graphene on SiO_2 substrate. (b) Height image; (c) zoomed-in image of (b); (d) fast Fourier transform filtered current image of region B. (e) Schematic illustration of the growth mechanism. (f) Raman spectra for h-MLG grains, BLG film and bare h-BN surface. (g) Moiré pattern of several grains. (h) AFM images of a peel-off graphene flake before and after c-PECVD. (i) AFM images of peel-off graphene flakes. (j) AFM images of the HGCs on SiO_2/Si after c-PECVD growth. (k) AFM image of a graphene membrane on SiO_2/Si

阵列的制备. Zhuo等人[22]利用第一种模式成功在SiO_2-Cu界面处制备了高质量石墨烯(图4(a)). 研究结果表明, 选用不同分子结构的含碳层会对石墨烯的质量造成显著影响, 平面分子结构的有机含碳层生长的石墨烯质量明显高于非平面分子结构有机含碳层生长的石墨烯. Su等人[26]利用第二种模式在多种绝缘衬底-Cu覆盖层界面处成功制备了石墨烯(图4(b)~(c)). 碳原子通过Cu晶界穿透到绝缘衬底表面, 并在其上形核和生长, 然后通过腐蚀掉金属Cu覆盖层, 获得了高质量的石墨烯. 不同于金属Cu, 金属Ni有较强的融碳能力. Kwak等人使[23]用Ni作为金属覆盖层, 利用石墨粉作为碳源, 在低温甚至室温条件下, 成功在SiO_2-Ni界面处制备了高质量石墨烯(图4(d)). 他们给SiO_2-Ni-C结构施加<1 MPa的均衡压力, 促使C原子通过Ni晶界穿透到SiO_2衬底表面, 然后在25~260℃的温度区间内退火1~10 min, 最后腐蚀掉Ni层获得了较高质量的石墨烯. 该方法将有助于不耐高温绝缘衬底上石墨烯的生长及器件应用.

4 金属蒸气辅助生长石墨烯

前述在绝缘衬底-金属覆盖层界面处生长石墨烯通常需要在后期通过刻蚀等方法去除金属层, 以获得绝缘衬底-石墨烯结构. 然而, 此过程往往会有金属残留或者对界面处石墨烯结构造成影响, 从而降低了石墨烯的质量. 为了解决这种问题, 研究人员提出了一种利用金属蒸气辅助生长的方法, 用于在绝

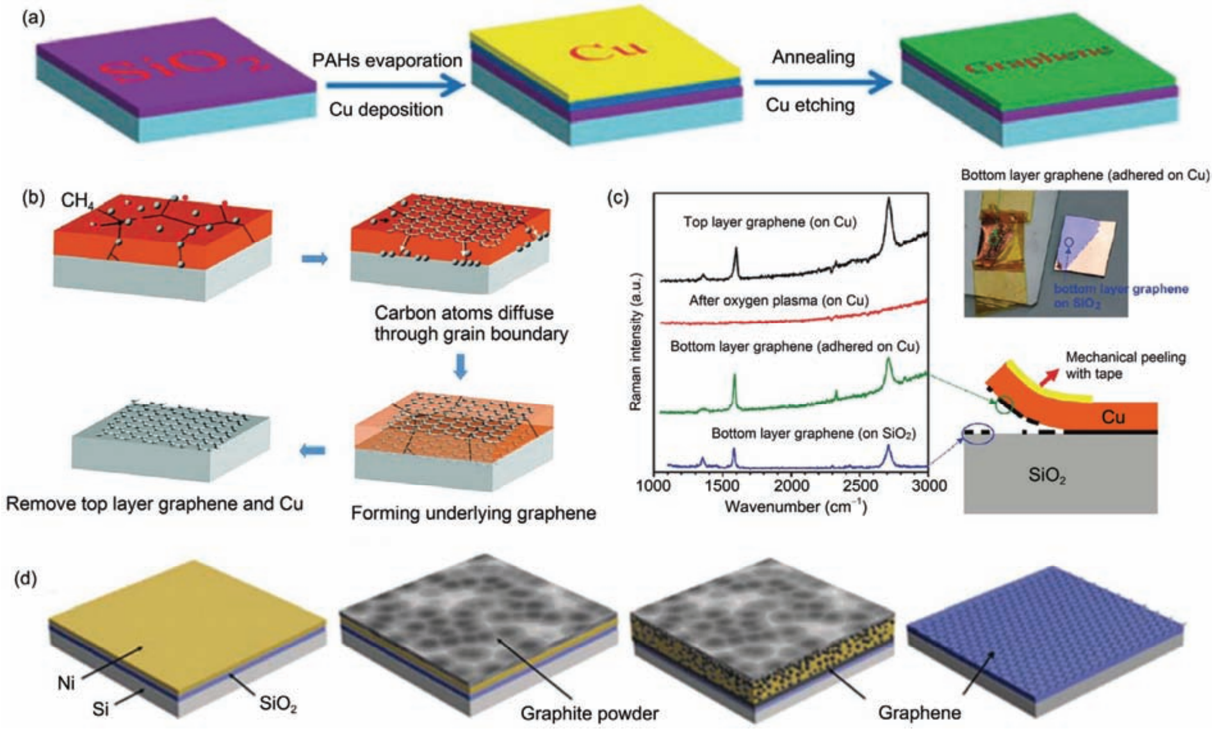

图 4 绝缘衬底-金属覆盖层界面处免转移生长石墨烯示意图与典型结果. (a) 铜催化SiO_2上直接生长石墨烯示意图. (b) 铜催化生长石墨烯示意图. (c) 不同条件下石墨烯的拉曼光谱. (d) 低温条件下扩散-辅助生长石墨烯示意图

Figure 4 Direct synthesis of transfer-free graphene on the interface of dielectric substrates and metal covering layer. (a) Schematic illustration of Cu catalyzed direct synthesis of graphene on SiO_2. (b) Schematic illustration of the Cu-catalyzed graphene growth. (c) The Raman spectra for graphene. (d) Schematic illustration of diffusion-assisted synthesis of graphene at low-temperature

缘衬底表面生长石墨烯.

目前为止, 已有包括Cu, Ga[27,54~57]蒸气在内的多种金属蒸气被成功用于生长石墨烯. Cu在常压下的熔点为1084.6℃, 在典型的CVD反应温度(1000℃左右)下, 很容易产生饱和Cu蒸气压[58]. Cu蒸气原子能与碳源气体分子充分接触并发生反应, 促进碳源气体的裂解, 从而加速绝缘衬底表面石墨烯的生长. 最早采用Cu蒸气辅助生长石墨烯的是韩国浦项科技大学Choi研究组[27]和中国台湾清华大学Chui研究组[56]. 如图5(a)~(f)所示, 他们分别利用Cu蒸气在SiO_2/Si上制备了高质量石墨烯. 通过优化Cu箔与衬底之间的距离, 可以得到较好的石墨烯质量. 相对于Cu而言, 熔点更低的Ga也被证明可以成功促进绝缘衬底表面的石墨烯生长[54,55]. 武汉大学付磊研究组[54]利用Ga蒸气成功在石英衬底上制备出了透明单层石墨烯, 并应用于超快除雾器(图5(g)~(i)). Murakami等人[55]也利用Ga蒸气辅助在绝缘衬底上制备了大面积石墨烯. 而且他们研究发现, 石墨烯的质量跟Ga蒸气的浓度正相关. 这些工作显著提高了免转移生长石墨烯的质量, 尤其是利用Cu蒸气辅助生长的石墨烯, 其质量更是与传统金属Cu上CVD生长的石墨烯相当, 将显著促进高性能石墨烯器件的应用和发展.

5 免转移生长石墨烯的器件应用

CVD石墨烯目前主要被用于制作场效应晶体管(FET)、逻辑器件、生物传感器、柔性显示屏、透明电极等. 绝缘衬底上生长石墨烯由于避免了转移工艺步骤, 有望在多个领域中实现高质量的石墨烯器件应用.

北京大学刘忠范研究组[33]利用他们在熔融态玻璃上生长的高质量石墨烯, 成功实现了智能加热玻璃器件以及热变色显示器件的制备(图6(a), (b)). 他们利用此石墨烯还实现了除雾器以及生物相容的器件制备, 扩宽了免转移石墨烯的应用领域. 除了石墨烯玻璃, 免转移生长的石墨烯还能直接用于FET器件的制备与性能测试. 图6(c)~(e)为利用在STO衬底上直接生长石墨烯制备的FET器件与相关性能测试结果, 显示了石墨烯器件具有较高的电学性能[32]. 武汉大学付磊课题组[54]利用Ga蒸气催化生长的石墨烯

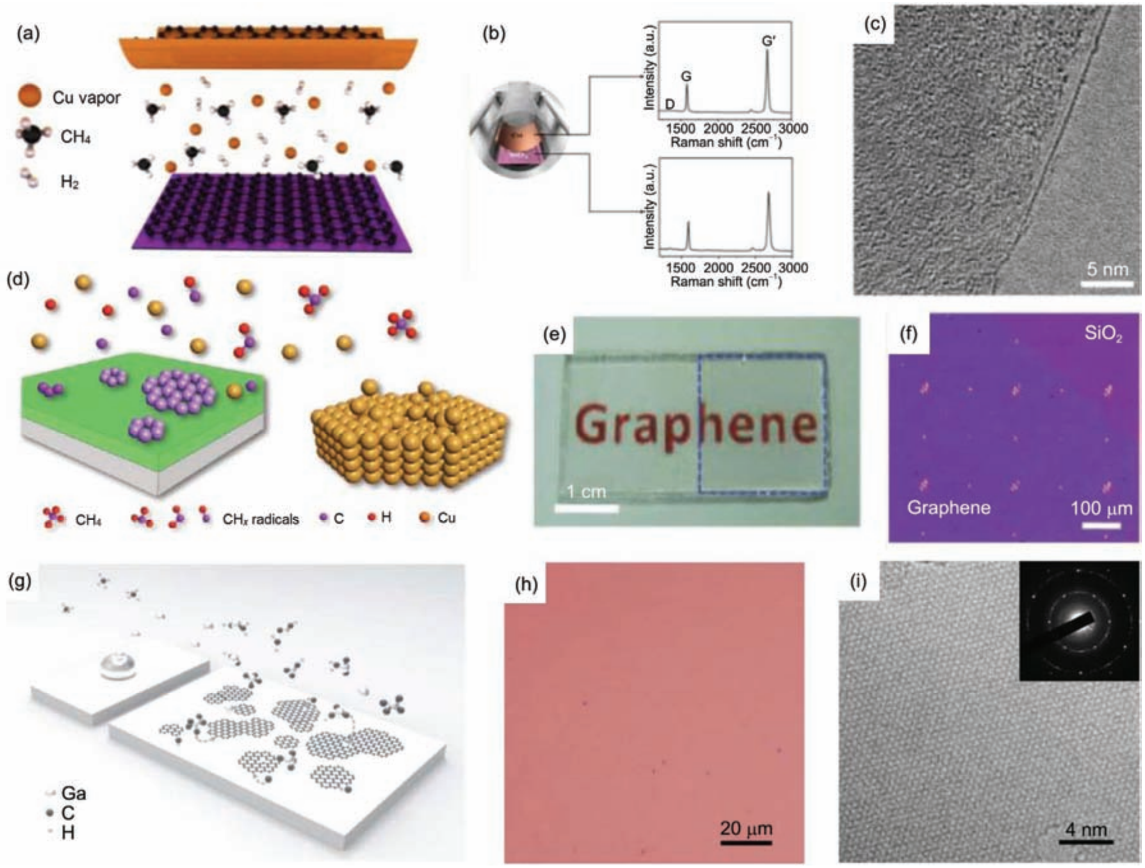

图 5 铜蒸气和镓蒸气辅助免转移直接生长石墨烯示意图与典型结果. 铜蒸气辅助同时在铜箔和SiO_2/Si衬底上生长石墨烯示意图(a)和拉曼光谱(b). (c) 转移后石墨烯的高分辨率TEM(HRTEM)图证明其为单层石墨烯. (d) 石墨烯的生长机制图. 在石英玻璃衬底(e)和SiO_2衬底(f)上直接生长石墨烯的示意图. (g) 镓蒸气辅助在石英衬底上直接生长石墨烯示意图. (h) 石墨烯薄膜转移到 300 nm SiO_2/Si衬底后的光镜(OM)图. (i) HRTEM及相应的选区电子衍射斑

Figure 5 Schematic and typical results of Cu vapor and Ga vapor assisted direct synthesis of graphene on dielectric substrates. Schematic illustration (a) and Raman spectra (b) of Cu-vapor-assisted CVD process inducing Cu-vapor-assisted growth of graphene on both Cu foil and underneath the SiO_2/Si substrate. (c) HRTEM image of transferred graphene examining the folded region that identifies single-layer graphene. (d) Schematic illustration of graphene growth mechanism. Direct deposition of graphene on fused quartz (e) and SiO_2 substrates (f). (g) Schematic drawing of Ga vapor-assisted CVD directly grown graphene on a quartz substrate. (h) OM image of a graphene film transferred on 300 nm SiO_2/Si substrate. (i) HRTEM image and the corresponding selected-area electron diffraction pattern

成功实现了超快除雾器器件的制备(图6(f)), 制备的除雾器能在32 V的安全电压下, 在6 s内完全除雾, 并且50个除雾循环后, 其性能依然没有降低. 除了用于与日常生活息息相关的领域, 绝缘衬底上生长的石墨烯也被用在微纳电子器件领域. 如图6(g)所示, Sun等人[59]用PECVD生长的纳米单晶石墨烯(NCG)成功制备了纳米机电系统开关(NEM). 这种器件具有优异的开关性能, 而纳米单晶石墨烯的生长机理以及更合理的纳米机电系统开关的结构设计需要进一步研究. 绝缘衬底上制备的石墨烯的广泛应用促进了石墨烯材料生长的进一步发展, 同时加速了石墨烯的产业化应用步伐. 虽然不同生长方法得到的石墨烯在结晶质量、工艺复杂度以及衬底选择等方面有或多或少的不足, 但依然能期待其将成为最有可能替代半导体硅的材料, 并在工业领域取得更广阔的应用.

6 总结与展望

近年来, 相对金属表面生长石墨烯, 绝缘衬底上石墨烯的生长以其不用转移的优势得到了充分关注, 大量新技术方案不断涌现并广泛应用于多种领域, 多篇有关绝缘衬底上直接生长石墨烯的综述也陆续发表[60~62]. 本文系统概述了最近几年发展起来的在绝缘衬底上生长石墨烯的方法, 按生长原理将其分

为: (1) 无催化辅助直接生长石墨烯; (2) 等离子体辅助低温生长石墨烯; (3) 绝缘衬底-金属覆盖层界面处生长石墨烯; (4) 金属蒸气辅助生长石墨烯. 同时对各种方法的优缺点进行了简要分析(表1). 最后, 本文介绍了绝缘衬底上生长石墨烯的相关应用.

尽管绝缘衬底上制备石墨烯取得了较大进展,

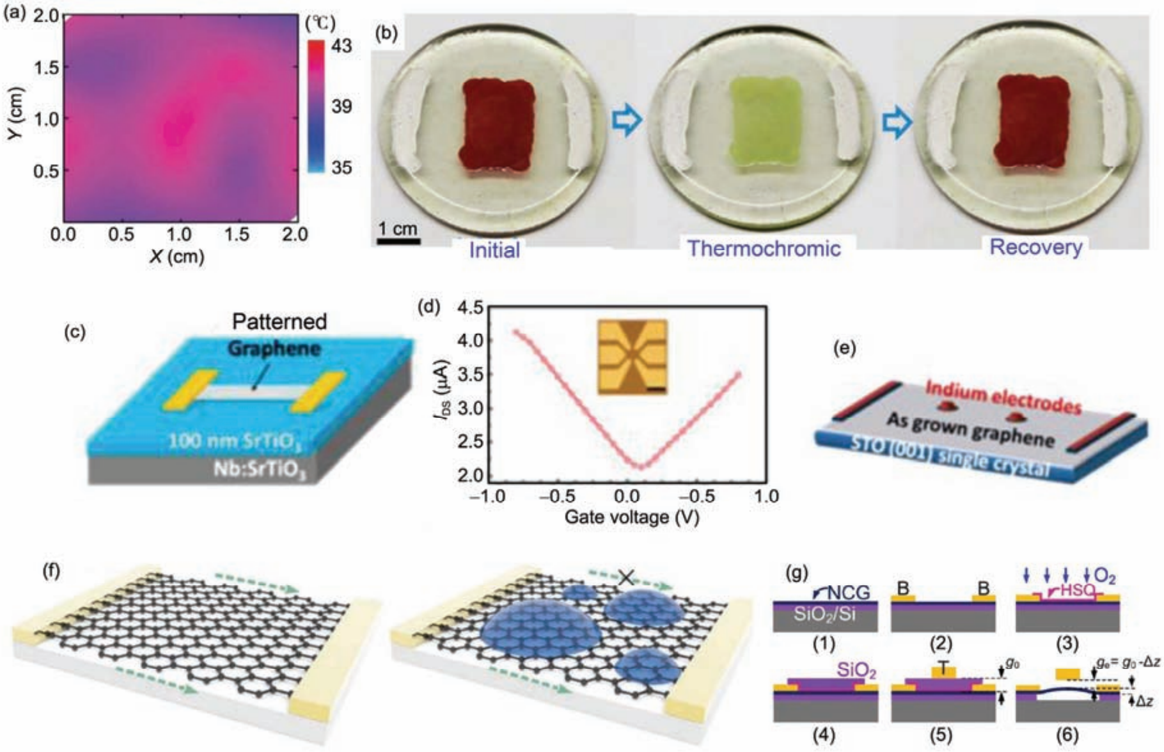

图 6 免转移石墨烯在多领域的应用示意图与典型结果. (a) 2 cm×2 cm的石墨烯玻璃在输入电压为 30 V时的表面温度等值线图. (b) 热变色性能照片. (c) Nb掺杂STO衬底上制备的石墨烯FET俯视图. (d) FET器件在VDS=0.01 V时的*I*-*V*曲线, 插图为单个器件的OM图, 标尺为 50 μm. (e) 基于石墨烯/STO器件的磁场传输特性测试示意图. (f) 直接生长的石墨烯完美地黏附在石英衬底表面. 直接生长石墨烯的上表面被水分子吸附, 而电流通过被石英衬底保护的下表面. (g) 基于NCG的NEM开关制备示意图. B和T分别代表下部和上部电极. g_0 为刻蚀前所设计的空隙, 其值由牺牲层的整体厚度决定

Figure 6 Schematic and typical results of transfer-free graphene applied in various applications. (a) Contour map of surface temperature on a 2 cm × 2 cm area of an as-grown graphene/glass sample under an input voltage of 30 V. (b) Photograph of the thermochromic display. (c) Schematic top-view of graphene FET fabricated on an STO/Nb-doped STO substrate. (d) Transfer curve of the FET device at VDS = 0.01 V in air. Inset: OM image of an individual device. Scale bar: 50 μm. (e) Schematic construction of graphene/STO based device for magneto-transport measurements. (f) Directly grown graphene films perfectly adhered on the surface of the quartz substrate. Upper surface of directly grown graphene absorbed by water molecules and the current carriers passing through the under surface protected by the quartz substrate. (g) Schematic of the NCG based NEM switch fabrication. B and T denote the bottom and top electrodes, respectively. g_0 is the designed air gap before etching, which is defined by the total thickness of the sacrificial layers

表 1 绝缘衬底上直接生长石墨烯的不同生长原理及其优缺点

Table 1 Growth mechanism, advantages and disadvantages of different graphene growth methods on dielectric substrates

生长原理	典型方法	优点	缺点	文献
无催化直接生长	热诱导碳源分解与形核生长	无催化剂，适用于多种衬底	生长速度慢，温度高	[24,25,30,32]
	特殊处理衬底及载气、源气	无催化剂，较高的生长速率与较大的晶核尺寸	生长温度高，需要匹配的衬底及源气	[29,31,35]
等离子体辅助低温生长	等离子体降低碳源裂解温度，促进石墨烯形核生长	生长温度低，速度快,适用于多种衬底	影响石墨烯质量，石墨烯的生长过程难以控制	[45~49]
绝缘衬底-金属覆盖层界面处生长	利用金属覆盖层的溶碳和催化能力，界面处生长石墨烯	生长速度快，窗口宽，适用于多种衬底	有金属接触，会导致金属残留，工艺复杂	[21~23,50~52]
金属蒸气辅助生长	金属蒸气远程催化	石墨烯质量高，生长速度快，无金属残留	生长温度相对较高，工艺复杂	[27,54~57]

然而在对石墨烯质量有更高要求的应用领域(如微电子器件应用等)，绝缘衬底上生长的石墨烯依然无法替代微机械剥离法制备的石墨烯以及部分金属衬底上CVD石墨烯．因此，进一步提高绝缘衬底上生长石墨烯的质量，对扩大其应用范围、推动石墨烯应用的发展至关重要．而只有充分理解了其生长机理，才有可能在绝缘衬底上生长出大面积高质量的石墨烯材料．我们相信，随着研究的不断深入，绝缘衬底上石墨烯的制备和应用将会得到更进一步的发展，石墨烯的工业化应用之路也将更加畅通．

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Summary for “绝缘衬底上石墨烯的化学气相沉积制备与器件应用”

Chemical vapor deposition of graphene on insulating substrates and its potential applications

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As the first two-dimensional crystal isolated in 2004, graphene has triggered numerous fundamental and technological studies because of its unique properties and a wide range of potential applications. To take these applications to an industrial level requires successful large scale growth of high quality graphene. Among popular methods for graphene synthesis, chemical vapor deposition (CVD) has received a lot of attention because of its relatively high yields, high quality and low cost in preparation of graphene. In addition, CVD is compatible with the existing silicon semiconductor processes, and exhibits potential for synthesis and applications of graphene at industrial scale. CVD graphene has been synthesized on various metal substrates such as ruthenium, iridium, platinum, nickel and copper. Though suitable for mass production, the need to transfer the graphene to different substrates has so far constrained its up-scaling to roll-to-roll production methods. However, CVD graphene on metal need transfer to insulating substrates for further device fabrication and characterization, and the extra transfer step inevitably causes the degradation of the graphene quality because of crack formation or resists residues. Researchers have developed some novel technologies aiming at reducing the influence of transfer process on the quality of graphene, but transfer process is still time-consuming and relatively expensive. An alternative to overcome the transfer difficulty is to synthesize graphene directly on insulating substrates. Epitaxial growth of graphene on single crystal SiC is one route towards mass production of graphene, however, single crystal SiC wafers are still very expensive. The search for better production techniques of graphene, in particular a transfer-free production method of high quality graphene, has intensified over the last few years. An amount of effective strategies have been utilized to realize the direct synthesis of high quality graphene on insulating substrates such as h-BN, silicon oxide, quartz, sapphire, $SrTiO_3$ and even normal glass. Due to the lack of catalytic capability and carbon-dissolving ability in insulating substrates, the direct growth of graphene often associates with the problems of high nucleation density, small domain size, poor layer control and slow growth rate. As such, more research works should be conducted to explore the growth mechanism on the insulating substrates.

In this paper, we reviewed recent progresses about direct growth of graphene on insulating substrates by chemical vapor deposition and its electronic applications. Firstly, we briefly discussed the newly progresses of graphene preparation and application. Great progress have been achieved in the field of direct synthesis of graphene on insulating substrates, however, there is still much room to improve further in many aspects, such as quality, domain size, layer and substrate suitability of graphene. We classified the growth strategies on insulating substrates into four groups: non-catalyst assisted method, plasma enhanced method, interface catalyzed growth and metal-vapor assisted growth. In each strategy, details of technology and merits were carefully discussed. In addition, we also introduced the typical applications of each strategy, which exhibits extraordinary prospect for improving our daily life. Finally, we shared our perspective views on future trend of this research field. We believe that with more and more efforts from the graphene-research community, technologies about direct synthesis of graphene on insulating substrates will be developed further. The future of directly grown graphene will become clearer in industrial applications.

graphene, chemical vapor deposition, insulating substrates, metal substrates, h-BN

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