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激光与光电子学进展

蓝宝石衬底上镍辅助的界面石墨烯生长

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摘要 基于AlN和GaN等Ⅲ族氮化物材料的第三代半导体照明器件具有广阔的应用前景，但常用的蓝宝石衬底散热差且与AlN、GaN存在较大的晶格失配和热失配，限制了该器件的推广应用。石墨烯是仅由碳原子组成的二维层状材料，层与层之间以范德瓦耳斯力结合，将其作为缓冲层能够缓解蓝宝石与Ⅲ族氮化物的失配问题。在蓝宝石基石墨烯缓冲层上外延AlN等氮化物后，利用石墨烯缓解蓝宝石衬底与AlN等Ⅲ族氮化物晶格失配较大的问题，有利于大功率发光二极管的制备。但石墨烯在绝缘衬底上的生长是一个难题。本课题组在蓝宝石衬底上镀金属镍层，然后利用镍辅助实现了蓝宝石衬底上石墨烯的生长，为利用石墨烯实现大功率半导体发光二极管打下了基础。

关键词 材料；石墨烯；镍；发光二极管；晶格失配；散热

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Graphene Growth at the Interface of Sapphire Substrate and Nickel Layer

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Abstract Semiconductor lighting devices based on Ⅲ-nitride materials, such as AlN and GaN, have broad application prospects, but the commonly used sapphire substrates have poor heat dissipation as well as large lattice and thermal mismatches with AlN and GaN, which limit their promotion and application. Graphene is a two-dimensional layered material comprising only carbon atoms. Graphene layers are combined with van der Waals forces. Using graphene as a buffer layer can alleviate the mismatch between sapphire and Ⅲ-nitride materials. AlN and other nitrides are grown on graphene-sapphire substrates. Graphene is used to alleviate the problem of large lattice mismatch between the sapphire substrate and Ⅲ-nitride materials, which is conducive to the preparation of high-power light-emitting diodes. However, the growth of graphene on an insulating substrate is difficult. In this study, a nickel layer is coated on sapphire substrates, and nickel is used to assist the growth of graphene on the sapphire substrate, which is helpful to realize high-power light-emitting diodes using graphene.

Key words materials; graphene; nickel; light-emitting diode; lattice mismatch; heat dissipation

OCIS codes 000.1570; 230.3670; 130.5990

1 引 言

最近几年，发光二极管(LED)的性能大幅提升，已被广泛应用于日常照明、特殊照明、杀菌等领域；然而，常用的蓝宝石衬底和外延层的晶格失配、热失配以及蓝宝石衬底热导率小、散热差的问题仍然是制约LED应用的主要障碍之一[1-14]。因此，提高蓝宝石衬底的散热性能和减少晶格失配成为一

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个重要的研究方向。目前，研究人员已提出了多种方法来解决LED的上述问题。其中的一种解决方案是将蓝宝石衬底上的LED外延层转移到具有高热导率的金属衬底上[5,7]，而激光剥离（LLO）是目前实现LED外延层转移最常用的技术。由于金属铜具有优异的导热性，转移后的LED的光输出功率比传统蓝宝石衬底上的LED增加了数倍[7]。然而，激光剥离的成本高、效率低，且不适用于宽带隙AlN，因此，需要一种成本更低且更有效的方法来代替该方法。范德瓦耳斯外延使得在石墨烯等二维（2D）材料上进行晶体生长成为可能，这种方法不需要外延层与衬底晶格完全匹配，降低了缺陷密度[15-17]。因此，一些基于石墨烯、氮化硼（BN）等的转移方法得到了广泛研究[8,18-21]。石墨烯层与层之间具有弱的范德瓦耳斯相互作用，可以很容易地将外延薄膜转移到目标衬底上[20-21]，如果利用这种方式把LED转移到高热导率的衬底上，就可以提高器件的散热性能。由此可见，如果在蓝宝石衬底上生长石墨烯，就可以利用石墨烯层间弱的范德瓦耳斯相互作用，将器件从蓝宝石衬底上剥离并转移到高热导率衬底上，从而解决器件的散热问题；同时，在石墨烯缓冲层上可以直接外延生长Ⅲ族氮化物，并且石墨烯缓冲层能弛豫部分晶格失配和热失配，有望解决LED与蓝宝石衬底晶格失配、热失配和散热性能不良的问题。本文提出了一种在蓝宝石衬底上生长石墨烯的方法，即：在金属镍的辅助下，通过常压化学气相沉积（APCVD）法在蓝宝石衬底上生长出石墨烯[22-23]。

2　石墨烯的生长

图1展现了在蓝宝石衬底上采用镍辅助生长多层石墨烯的示意图。首先将蓝宝石衬底（c面）依次在丙酮、酒精和去离子水中进行超声清洗，然后采用电子束蒸发沉积数百纳米厚的镍膜（通常为400 nm或300 nm，在此厚度下生长的石墨烯质量最好），如图1（b）所示。之后采用常压化学气相沉积（APCVD）法生长多层石墨烯。将带有镍膜的蓝宝石衬底置于水平石英管式炉中并加热至1100 ℃，加热速率控制在约10 ℃/min，并在退火过程中引入280 mL/min氩气和100 mL/min氢气的混合气流；温度达到1100 ℃时，将5 mL/min甲烷作为碳源引入炉管中，氩气流量约为200 mL/min；生长时长通常为30 min，然后将样品以50～100 ℃/min的速率快速冷却至室温。图1（c）显示了在镍上表面获得的多层石墨烯。然后，使用氧等离子体（600 s，50 W）清除镍上表面的石墨烯；再用$FeCl_3$溶液（质量分数为20%）刻蚀镍层（根据拉曼光谱可确认镍表面的石墨烯已被全部消除）。图1（d）所示的石墨烯直接生长在镍层和蓝宝石衬底的界面上，避免了复杂且技术要求较高的石墨烯转移过程。

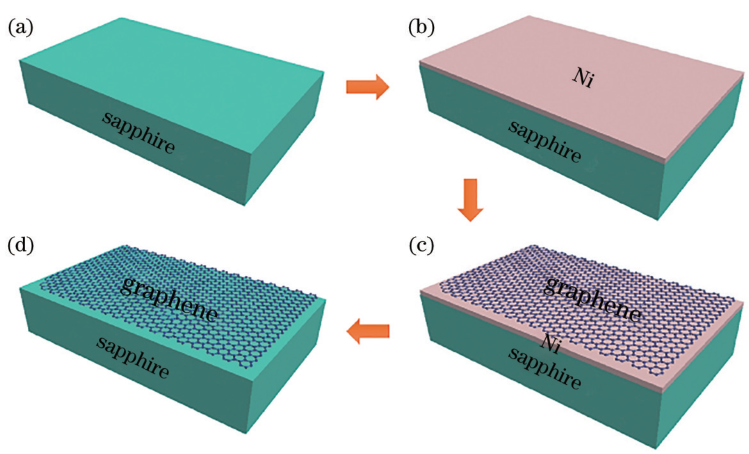

图1　蓝宝石衬底上多层石墨烯生长方法示意图。（a）制备蓝宝石衬底以合成石墨烯；（b）通过电子束蒸发将镍沉积在蓝宝石衬底上；（c）生长后，在镍蓝宝石衬底的顶面上形成多层石墨烯；（d）在表面进行氧等离子体处理，清除镍表面的石墨烯，然后刻蚀掉镍，可以发现镍和c面蓝宝石界面处生长出多层石墨烯

Fig. 1　Schematics of a method for growing few-layer graphene on sapphire substrate. (a) Sapphire substrate (c-plane) is prepared to synthesize graphene; (b) nickel is deposited on sapphire substrate by electron beam evaporation; (c) after growth, few-layered graphene forms on nickel's top surface of sapphire substrate; (d) after O_2 plasma treatment on the surface and then etching away the nickel, few-layer graphene grown on the interface between nickel and c-plane sapphire can be found

3 石墨烯表征与分析

图 2 显示了镍刻蚀前后蓝宝石衬底上石墨烯的表征结果。图 2(a)中的曲线 1 为镍层上表面多层石墨烯的典型拉曼光谱图，其中 G 峰和 2D 峰分别位于 1583 cm^{-1}左右和 2719 cm^{-1}。图 2(b)为镍层上表面石墨烯的扫描电子显微镜(SEM)图像。用氧等离子体(24 Pa，50 W)处理镍层上表面 6 min 后进行拉曼光谱测试，结果如图 2(a)中的曲线 2 所示。很显然，拉曼光谱中没有明显的峰，这表明镍上表面的石墨烯已经被清除干净。

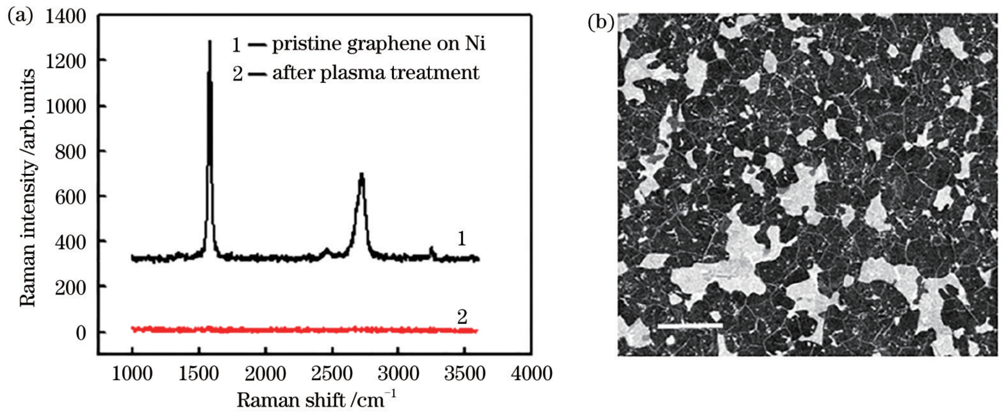

图 2 镍层上表面石墨烯的表征。(a)氧等离子体处理前(曲线 1)后(曲线 2)镍层上表面石墨烯的拉曼光谱；(b)镍层上表面石墨烯的SEM图像，比例尺为 3.5 μm

Fig. 2 Characterization of graphene on the surface of nickel film. (a) Raman spectra of graphene on the surface of nickel film before (curve 1) and after (curve 2) oxygen plasma treatment; (b) SEM image of graphene on the surface of nickel film, scale bar is 3.5 μm

图 3(a)显示了在等离子体处理和刻蚀掉镍之后的蓝宝石衬底上多层石墨烯的拉曼光谱，该石墨烯并非源自镍层的上表面，而是原镍层与蓝宝石界面处生长的石墨烯。该石墨烯的拉曼光谱与表面石墨烯表现出相似的特征，且具有明显的 D 峰，此石墨烯的 D 峰、G 峰和 2D 峰分别位于 1351，1596，2687 cm^{-1}处。因此，验证了本课题组在蓝宝石衬底上生长出了多层石墨烯。

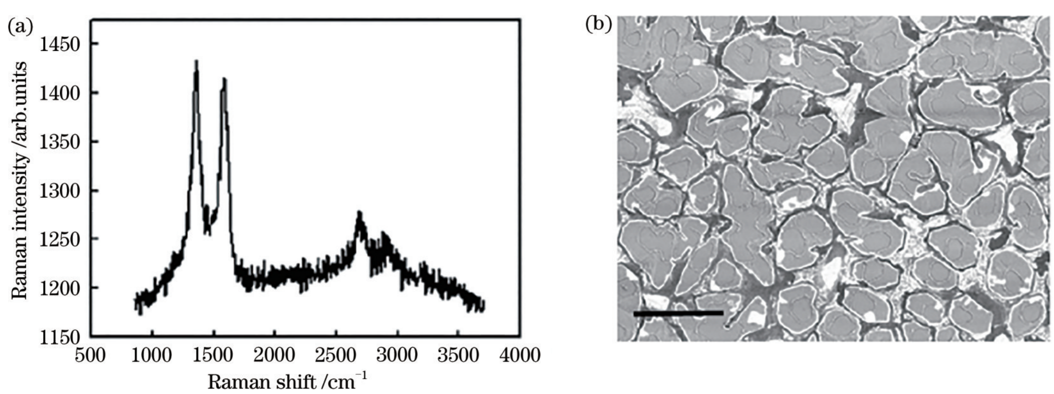

图 3 界面石墨烯的表征。(a)氧等离子体处理和刻蚀掉镍后，镍层和蓝宝石衬底界面上多层石墨烯的拉曼光谱；(b)镍层和蓝宝石衬底界面上石墨烯的 SEM 图像，比例尺为 20 μm

Fig. 3 Characterization of graphene at the interface. (a) Raman spectra of graphene on the interface between nickel film and sapphire substrate after oxygen plasma treatment and etching away the nickel; (b) SEM image of graphene on the interface between nickel film and sapphire substrate, scale bar is 20 μm

镍衬底上石墨烯的生长机制为表(界)面偏析机制。在该机制下，解离的碳原子在高温下溶入到金属体相中，降温时从体相中析出，在镍层表面或镍层与蓝宝石界面形成石墨烯。以该种机制生长的石墨烯的层数难以控制，最后形成了不均匀的多层石墨烯。

4 结　　论

基于AlN、GaN等Ⅲ族氮化物材料的第三代半导体照明器件具有广阔的应用前景，但常用的蓝宝石衬底散热差且与AlN、GaN存在较大的晶格失配和热失配，从而限制了该器件的推广应用。石墨烯是仅由碳原子组成的二维层状材料，层与层之间以范德瓦耳斯力结合，将其作为缓冲层能够缓解蓝宝石与Ⅲ族氮化物的失配问题。本课题组利用金属镍辅助，在水平石英管式炉中用常压化学气相沉积方法生长多层石墨烯，即：将带有镍层的蓝宝石衬底加热至1100 ℃，利用甲烷作为碳源，在1100 ℃的温度下生长30 min，然后将样品快速冷却至室温。该方法在镍层上表面获得了多层石墨烯，同时在镍层和蓝宝石的界面处也得到了多层石墨烯，解决了石墨烯在绝缘衬底上生长的问题，避免了复杂且技术要求高的石墨烯转移过程，为利用石墨烯实现第三代大功率半导体照明器件打下了基础。

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