基于模板剥离法制备有机晶体发光二极管器件及其特性

周威^①, 董奉喜^①, 丁然^{①②*}, 冯晶^①

① 吉林大学电子科学与工程学院, 集成光电子国家重点实验室, 长春 130012;

② 长春理工大学, 国家纳米操纵与制造国际联合研究中心, 长春 130022

* 联系人, E-mail: dingran12@mails.jlu.edu.cn

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摘要 有机晶体材料由于具有低的杂质含量、高的载流子迁移率、以及高的荧光量子效率在光电器件领域受到人们广泛的关注. 但是, 由于有机晶体材料具有易碎、致柔且对有机溶剂敏感等特性, 导致其难于制备发光二极管器件. 本文设计了一种简单且无破坏性的工艺方法, 即模板剥离法, 制备有机晶体发光二极管器件. 基于此方法通过改善晶体与电极之间的接触, 可使载流子均匀注入晶体有源层, 从而获得了均匀电致发光的二极管器件.

关键词 有机晶体, 噻吩/苯齐聚物晶体, 发光二极管, 模板剥离法, 边发射电致发光

有机晶体材料由于具有规则的分子排列、低的杂质含量、高的载流子迁移率以及高的荧光量子效率等优点在光电器件领域受到人们的重视, 例如有机场效应晶体管^[1~4]、光泵激光器^[5~8]、发光二极管^[9~12]等. 自从Pope等人^[13]首次报道了利用蒽晶体材料制备的电致发光器件之后, 在光电器件领域得到长足发展并表现出优秀的光学和电学特性. 例如在部分晶体内观测到放大自发辐射(ASE)现象, 被认为是最有希望实现有机电泵激光的材料; 其较高的载流子迁移, 可满足电泵激光器在较高电流密度和激子密度下工作, 同时其较高的荧光量子效率弥补了由于电荷诱导吸收和激子猝灭引起的材料在高激发密度下发光效率降低的损失. 因此, 有理由相信基于此类晶体材料制备的电致发光器件最有希望实现有机电泵激光器, 但是利用晶体材料制备高性能的发光二极管器件的报道却寥寥无几. 这是因为存在一些内在因素一直限制了其在发光二极管器件方面的应用, 例如晶体内部空穴和电子的迁移率不匹配、无法精确

控制晶体的厚度, 并且有机晶体自身易碎、致柔和对有机溶剂敏感等. 在之前的研究中, 人们常采用一种黏附法来制备有机晶体发光二极管器件, 将生长好的晶体材料转移到蒸镀阳极的衬底表面, 依靠范德华力的作用使晶体与电极相接触, 这种依靠微弱的作用力相接触的方法阻碍了载流子的注入, 并且在高电流密度下会导致器件极易击穿^[9~12].

为了解决器件中的晶体与电极间的接触问题, 本文采用了一种简单且无破坏性的方法——模板剥离法. 模板剥离法曾被用于制备具有超平滑金属薄层和具有等离子体效应的超材料^[14,15], 并利用此方法成功制备了可弯曲的发光二极管器件和光电池等^[16,17]. 在此方法的基础上, 可以通过真空蒸镀的方式直接蒸镀二极管器件的阴极和阳极到有机晶体的上下两面, 实现晶体与电极之间更紧密的接触, 可有效提高载流子的注入效果, 同时可从制备的有机晶体发光二极管中观测到均匀的电致发光现象. 此外, 由于晶体内部具有规则的分子排布, 晶体具有很强的自波

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导效应, 导致器件有很明显的边发射电致发光特性.

1 晶体发光二极管器件的制备方法

(i) 晶体生长方法. 选用纯度为99%的2,5-双(4-联苯基)双噻吩(BP2T)有机小分子材料, 并基于物理气相输运法利用双温区管式炉生长有机晶体材料, 炉中有2个可控温区, 1个高温升华区, 1个低温结晶区. 原材料BP2T处于高温升华区, 温度设为380℃, 分子在高纯氩气流的带动下向低温区输运, 氩气流速调节至40 mL/min; 被输运的分子将在低温区结晶生长有机晶体材料, 低温区的温度为340℃. 晶体具有均匀光滑的表面, 厚度在200~500 nm之间, 面积可达3 mm × 3 mm.

BP2T晶体材料具有很高的荧光量子效率^[18,19], 晶体内部分子的规则排布导致晶体具有很强的自波导特性, 荧光显微镜照片(图1)可以观测到晶体边缘发射很强的黄绿色荧光. 对于BP2T分子来说, 其跃迁偶极的方向基本沿着分子的长轴方向, 在晶体内部, 分子的长轴方向与晶体的 ab 面的法线之间仅有1.2°夹角, 晶体内部跃迁偶极矩几乎垂直于晶面, 所以光在晶体内部传播时会垂直于跃迁偶极的方向, 进而向晶体边缘传导, 形成很强的自波导特性^[20~22].

(ii) 模板剥离法制备发光二极管器件. 具体制备步骤如图2所示. (1) 将生长的有机晶体从双温区管式炉中转移到带有二氧化硅层的硅衬底表面; (2) 利用真空蒸镀的方法在晶体表面掩膜蒸镀一层100

nm厚金电极作为阳极; (3) 在蒸镀阳极的晶体表面中心滴加1滴NOA63光刻胶(Norland); (4) 在液滴上盖1片厚度为0.6 mm的透明玻璃片. 在毛细力的作用下, 光刻胶会沿着器件表面向边缘扩散, 最后覆盖整个器件. 光刻胶薄层的厚度由玻璃自身重量决定, 约在0.3~0.8 mm; (5) 利用125 W的紫外灯曝光18 min, 待光刻胶发生聚合后, 利用小刀片将玻璃与硅片相分离. 由于玻璃的黏附力比硅衬底更强, 所以光刻胶会被转移到玻璃衬底上, 同时带有阳极及晶体的二极管器件也将被剥离下来, 并被转移到光刻胶衬底上; (6) 在剥离下来的器件另一侧晶体表面蒸镀10 nm厚钙和20 nm厚的银电极作为阴极, 进而制备了三明治结构的晶体发光二极管器件. 电极是在 5×10^{-4} Pa的高真空环境中、以1 Å/s的速度通过真空蒸镀法沉积上的, 器件的有源区面积由金属掩膜板尺寸(200 $\mu\text{m} \times 300 \mu\text{m}$)决定.

基于模板剥离法制备的有机晶体材料发光二极管器件, 在制备过程中通过转写的方式将晶体器件转移到光刻胶黏附的玻璃衬底上, 避免引入机械硬伤对晶体表面的破坏, 有效保护晶体有源层的完整性. 同时, 器件阴极和阳极可通过真空蒸镀的方法蒸镀到晶体两侧表面, 可有效解决金属与电极之间的接触问题, 提高载流子的注入效果, 保证其可以均匀地注入到晶体有源层内部.

2 基于BP2T晶体材料的发光二极管器件

2.1 晶体二极管器件表征

对利用模板剥离法制备的BP2T晶体发光二极管器件进行光电特性表征, 器件的阳极和阴极分别通过真空蒸镀的方法蒸镀到晶体的上下表面, 确保晶体与电极之间具有紧密的接触并益于载流子的注入. 同时, 分别利用金属材料金作为阳极和钙/银作为阴极, 其功函数分别为4.7和2.87 eV, 而BP2T晶体分子占据的最高轨道(HOMO)和最低轨道(LOMO)分别估计为4.8和2.8 eV^[18,19]. 因此, 形成良好的能级匹配, 从而确保空穴和电子可有效地注入晶体内部.

随着电流密度的增大, BP2T晶体发光二极管器件的电致发光强度逐渐增强. 图3(a)~(c)表明, 发光二极管器件具有很强的边发射光的特点, 随着电流密度的增大, 其边发射光强度逐渐增强. 分析边发射的原因, 存在2种机制: (1) 电极形成的镜面反射效

图1 (网络版彩色)(a) BP2T分子式; (b) BP2T晶体荧光显微镜照片; (c) 晶体内分子的空间排布

Figure 1 (Color online) (a) Chemical structure of BP2T; (b) fluorescence photograph of BP2T; (c) crystal packing of BP2T

图 2 (网络版彩色)模板剥离法制备晶体发光二极管器件简要步骤
 Figure 2 (Color online) Schematic of the template stripping process

应. 由于器件两侧电极采用金属电极, 顶电极采用10 nm厚钙和20 nm厚的银电极作为阴极, 属于半透明电极, 光在从顶电极射出时会有部分光被反射后, 在晶体内部向器件边缘传导; (2) 由晶体自身自波导性质引起. 由于BP2T分子的跃迁偶极方向沿着分子的长轴方向, 同时, 分子排布几乎垂直于晶体表面, 光在晶体内部传播并被限制在晶体内部, 这导致了晶体具有很强的自波导效应^[23]. 在2种机制共同作用下, 能观测到明显的边发射光的现象. 图3(d)表明, 沿器件法线方向测试了器件的电流密度-电压-亮度特性曲线, 开启电压在1 V左右. 当电压在13 V左右时, 观测到均匀的电致发光现象, 由于电极和晶体之间紧密的接触和能级匹配导致了低的开启电压. 器件的电致发光强度随着电流密度的增加而增强, 当电流密度达到1933 mA/cm²时, 器件的发光亮度达到16.87 cd/m². 随着电流密度的增大, 测得的电致发光光谱强度也逐渐增强(图3(e)). 但是器件的电致发光效率依然很低, 这是因为BP2T晶体中空穴和电子迁移率的不同导致了复合发光的载流子不匹配, 并且器件边缘发光也降低了器件的发光效率.

2.2 对比黏附法制备的发光二极管器件性能

对比模板剥离法和黏附法制备的晶体发光二极管器件的电流电压特性曲线, 结果表明, 模板剥离法有效改善了器件中电极与晶体之间的接触, 载流子注入效果更好, 并且发光更均匀, 器件的性能更好. 从图4可以看出, 由模板剥离法制作的有机发光二极管具有较高的电流密度和较低的阈值电压, 进一步证明了紧密的电极与晶体的接触可以产生更有效的载流子注入. 利用黏附法制备的晶体发光二极管仅在高驱动电压下观测到不均匀的边发射光特性, 并能观察到很大一块不发光区域和破损点. 这是因为依靠范德华力使晶体和电极接触, 电极材料粗糙的表面导致了不完整的接触平面, 从而产生不均匀发光, 并且在高电压下, 不均匀的载流子注入导致器件极易被击穿.

3 结论

本文首次将模板剥离法引入有机晶体材料发光二极管器件制备中, 并成功制备了基于BP2T晶体材料的发光二极管器件. 黏附法制备的发光二极管器

图3 (网络版彩色)(a)~(c) BP2T晶体发光二极管器件电致发光照片,工作中的发光器件所处的驱动电流分别为 117, 223 和 328 mA/cm²; (d) 电流-电压-亮度特性曲线,插图为制备的发光二极管器件光学显微镜下照片; (e) 电致发光光谱图及荧光光谱对比曲线

Figure 3 (Color online) (a)–(c) Photographs of BP2T single crystal-based organic light-emitting diodes (OLEDs) under operation at different driving current of 117 (a), 223 (b) and 328 (c) mA/cm², respectively; (d) current-voltage-luminescence characteristics of BP2T-OLEDs, inset is the photograph of crystal-based OLEDs; (e) electroluminescence spectra of BP2T-OLEDs at various current density and photoluminescence spectrum of BP2T single crystal as reference

图4 (网络版彩色)模板剥离法和黏附法分别制备晶体发光二极管器件的电流-电压特性曲线对比图;内插图为黏附法制备器件开启和关闭后的显微镜照片

Figure 4 (Color online) The comparison of current density-voltage characteristics of the devices between the template stripping technique and the laminating method. The inset shows the crystal-based OLEDs under operating of turn-on and turn-off fabricated by laminating method

件中,晶体与电极之间依靠范德华力相接触,导致局部载流子注入不均匀,极易造成器件击穿或破损,严重影响器件的性能和稳定性.然而,基于模板剥离法器件的阴极和阳极可通过真空蒸镀的方法分别蒸镀到晶体两侧,可有效解决晶体与电极之间的接触问题,实现晶体与电极紧密接触,使载流子注入更均匀,器件可观测到均匀的电致发光现象.此方法可普遍适用于二维片状晶体,由于电极掩膜板等限制条件,实验中常选用表面积在3 mm×3 mm以上的晶体材料,同时控制晶体的厚度,选用500 nm以下厚度的晶体材料,为实现高性能发光二极管器件提供有利条件,同时也为今后实现有机电泵激光打下一定基础.但是,晶体材料在光电器件领域的应用还有很长的路要走,其电致发光亮度低、功率效率低和开启电压高等问题仍亟待解决,希望随着晶体材料的进步,以及器件制备方法和性能方面的提高,能为光电器件发展提供重要的输入.

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Organic single crystal-based light-emitting devices by template stripping technique

ZHOU Wei¹, DONG FengXi², DING Ran^{1,2} & FENG Jing¹

¹ State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China;

² Changchun University of Science and Technology, International Research Centre for Nano Handling and Manufacturing of China (CNM), Changchun 130022, China

Organic single crystals have attracted extensive interests in the field of optoelectronic and electronic devices for their high chemical purity, high charge-carrier mobility and high luminescent quantum efficiency. The motivation for research on organic single crystals is their highly arranged packing structure, which provides an ideal model to investigate the basic interactions between the molecules and stacking modes and optoelectronic performance. Because of advantages of these crystals, they have been employed in much functional optoelectronic devices such as organic field-effect transistors (OFETs), light-emitting organic field-effect transistors (LE-OFETs), optically pumped lasers, photovoltaic cells and so on. However, the reports on organic single crystal based organic light emitting devices (OLEDs) are scarce. There is a big difficulty in the fabrication of organic single crystal-based OLEDs because of their intrinsic properties like soft, fragile and sensitive to organic solvent. In this work, a simple and non-destructive method template stripping has been applied into the single crystal-based OLEDs to improve the contact problem and realize its bright emission. Based on this method, the physical vapour transport grown crystals are firstly transferred to the modified silicon substrate. Then an anode of 100 nm gold film is deposited on the top of the crystal surface by thermal evaporation with metal mask. After dropping a microliter of photoresist polymer on the device, a glass is pressed on top by its own weight. And the polymer will spread to the edge of the glass and totally cover the device. Then it will be cured after exposed to a UV-light source with a power of 500 W. The device will be transferred to the glass with the help of a knife for separation. Finally the cathode of Ca/Ag will be evaporated on the other side of crystal. The sandwiched structure devices can be achieved by this method. Both anodes and cathodes of the crystal-based OLEDs can be deposited onto the opposite surface of the organic single crystals by thermal evaporation on both sides, so that a much improved contact between the crystals and the electrodes can be realized, which enhance the carrier injection into the active layer. Homogenous light emission can be observed from these crystal-based OLEDs. And the molecules of BP2T are arranged layer by layer which are nearly perpendicular to the crystal plane. As we known, the directions of the transition dipole moments lie along the long axis of the molecule. The light in the crystal will transmit to the edge of the crystal which recognized as self-waveguide effect. In the same way, edge-emitting can be seen from the crystal-based OLEDs which attributed to this self-waveguide. In order to clarify the template stripping method can work well on the fabrication of single crystal based OLEDs. We compare the performance of both devices between the lamination method and template stripping method. Based on lamination method, the single crystals are simply laminated onto the top of the anode by van der Waals force which results in an incomplete contact. Compared to the lamination method, the devices show higher carrier injection and low voltage threshold by this compacted contact between crystals and electrodes without any breakages. It is expectable that this technique would support broad applications of the organic single crystals in the crystal-based optoelectronic devices.

organic single crystal, thiophene/phenylene co-oligomers, organic light-emitting diode, template stripping technique, edge-emission

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