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宁　夏　大　学

专业学位论文

准二维钙钛矿发光二极管的制备与性能优化

**Fabrication and optoelectric performance optimization of quasi-two-dimensional perovskite light-emitting diodes**

学 位 申 请 人： 李梦瑶

指导教师： 李国龙副教授

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摘要

有机-无机杂化钙钛矿具有色纯度高，带隙可调节，制作成本低和方法简单，有希望称为下一代半导体材料，被广泛应用于发光二极管、太阳能电池和探测器等领域。三维钙钛矿发光二极管（Light emitting device, LED）发光层成膜质量不高、稳定性差，而准二维钙钛矿薄膜具有独特的多重量子阱结构和光电性能逐渐走进人们的视线。准二维钙钛矿发光二极管具有稳定性好、激子结合能高等特点，但是仍然有有机长链导电性差、相纯度不易受控制等难题需要解决。

基于上述研究现状和研究目的，我们进行了两个实验方案的研究：通过甲脒基阳离子和甲胺基阳离子化学计量比混合，高温二次退火提高准二维钙钛矿发光二极管的发光亮度和发光效率。本论文主要研究准二维钙钛矿发光二极管的光电性能优化，论文的主要研究工作如下：

1. 通过对准二位钙钛矿前驱液中A位离子中的甲脒基阳离子(FA+)和甲胺基阳离子(MA+)化学计量比的调控，获得了混合阳离子钙钛矿薄膜，研究了薄膜中混合阳离子对成膜质量、结晶质量、光学性质和电学性质的影响。确定了MA+：FA+=7.5:2.5可以达到发光二极管的最佳性能，并对其进行了性能表征和比较。最终得到了亮度高达11596 cd·m-2的PEA2(MA0.75FA0.25PbBr3)9PbBr4钙钛矿发光二极管，可达到基于纯PEA2(FAPbBr3)9PbBr4钙钛矿发光二极管的1.67倍，混合阳离子后钙钛矿LED的最大电流效率 (Current efficiency, CE )也从6.26 cd·A-1提升到10.32 cd·A-1。
2. 基于钙钛矿薄膜的结晶生长动力学理论，优化钙钛矿薄膜一步溶液法生长工艺。钙钛矿光电器件的性能对薄膜的形貌、结晶质量及光学性质显示出极大的依赖性。通过测试高温二次退火对钙钛矿薄膜形貌的优化以及光电性能的提高，探索了钙钛矿的光电性能对结晶质量的依赖性。增加一步80℃退火可以使钙钛矿n=15的准二维钙钛矿薄膜在结晶过程中晶粒更加缓慢的生长，形成更致密的薄膜。动态和稳态光致发光测试随后表明，增加二次退火步骤可以有效的增加平均载流子寿命和PL强度，并最终得到的准二维钙钛矿LED的亮度高达25408 cd·m-2，并具有18.74cd·A-1的最大CE。

关键词：准二维钙钛矿，混合阳离子，二次退火，结晶

**Abstract**

Organic-inorganic hybrid perovskites with high color purity, tunable band gap, low fabrication cost and simple fabrication method, are consider as promising next-generation semiconductor materials, which is widely used in the fields of light-emitting diodes, solar cells and detectors. However, in the three-dimensional perovskite light-emitting diode, light-emitting layer has low film quality and poor stability, quasi-two-dimensional perovskite thin films with unique self-assembled multiple quantum well structure and optoelectronic properties have gradually achieved great success in perovskite light-emitting diodes. Quasi-two-dimensional perovskite light-emitting diodes have the characteristics of good stability and high exciton binding energy. Unfortunately, quasi-2D PeLEDs suffer from severe efficiency roll-off, which manifests that EQEs start to significantly drop at relatively low current density. Corresponding reasons can be attributed to long-chain organic conductivity, uncontrollable phase purity and strong Auger recombination.

Based on the above research status and research purposes, we conducted two aspects of experimental studies: through the stoichiometric mixing of formamidinium-based cations and methylamine-based cations, high-temperature secondary annealing improves the brightness and current efficiency of quasi-two-dimensional perovskite light-emitting diodes. This paper mainly studies the optoelectronic performance optimization of quasi-two-dimensional perovskite light-emitting diodes. The main research work of the paper is as follows:

1. By aligning the stoichiometric ratio of formamidinium cations (FA+) and methylamine cations (MA+) in A-site ions in the binary perovskite precursor solution, mixed cation perovskite films were obtained. And effects of mixed cations on film-forming quality, crystalline quality, optical and electrical properties were explored. It was determined that MA+: FA+=7.5:2.5 can achieve the best optical and Electrical performance of light-emitting diode, and its performance was characterized and compared. Finally, a PEA2(MA0.75FA0.25PbBr3)9PbBr4 perovskite light-emitting diode with a brightness of up to 11596 cd·m-2 was obtained, which can reach 1.67 times that of the pure PEA2(FAPbBr3)9PbBr4 perovskite light-emitting diode. The maximum current efficiency (CE) of the perovskite LED was also improved from 6.26 cd·A-1 to 10.32 cd·A-1.
2. Based on the theory of crystal growth kinetics of perovskite thin films, the one-step solution growth process of perovskite thin films was optimized. The performance of perovskite optoelectronic devices shows a great dependence on the morphology, crystalline quality and optical properties of the thin films. By testing the optimization of the morphology of perovskite thin films and the improvement of the optoelectronic properties of perovskite films by high-temperature secondary annealing, the dependence of the optoelectronic properties of perovskite on the crystalline quality was explored. An additional step of annealing at 80 ℃ can make the quasi-two-dimensional perovskite film with perovskite n=15 grow more slowly during the crystallization process and form a denser film. Dynamic and steady-state photoluminescence tests subsequently showed that adding a secondary annealing step can effectively increase the average carrier lifetime and PL intensity, and the resulting quasi-2D perovskite LED has a brightness as high as 25408 cd·m- 2, and has a maximum CE of 18.74cd·A-1.

Key words: Quasi-2D perovskites, mixed cations, secondary annealing, crystallization

1. 绪论
   1. 课题研究背景

随着科技的高速发展与人们对美好物质的需求逐渐增加，显示照明领域也在逐渐发展。从十九世纪让人类社会迈入电气照明时代的戴维的电弧灯到爱迪生的白炽灯在生活中普遍应用，