多元铜基硫族半导体纳米晶的发光性能及其在电致发光器件中的应用进展

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摘要 半导体纳米晶(又称为半导体量子点)由于其色纯度高和尺寸依赖的发光性能等优势, 在照明和显示方面受到了科学界和产业界的广泛关注。目前, 基于半导体量子点的电致发光器件所使用的发光材料以镉基硫族化合物量子点为主, 然而镉元素对环境和人体都有一定的危害。因此, 开发一种环境友好且光电性能良好的无镉半导体纳米晶是非常必要的。近年来, 多元铜基硫族半导体纳米晶由于其毒性低、组分可调的发光特性及其在光电子器件领域的潜在应用受到了广泛关注。本文详细综述了多元铜基硫族半导体纳米晶的组分、表面配体、晶体结构和纳米结构等因素对其发光特性的影响, 着重阐述了多元铜基硫族半导体纳米晶在电致发光器件中的研究进展, 最后对多元铜基硫族半导体纳米晶的发展进行了展望。

关键词 半导体纳米晶, 多元铜基硫族化合物, 发光性能, 电致发光器件

半导体纳米晶又称为半导体量子点, 由于其具有独特的尺寸依赖的发光性质和窄而对称的发光光谱, 在生物标记和光电器件等领域展现出巨大的应用潜力^[1-6]。在过去的几十年中, 以镉基硫族化合物为代表的II-VI半导体量子点由于其成熟的合成技术和优异的光电性能在电致发光器件方面取得了重大突破, 其器件效率指标可与传统的有机电致发光器件相媲美^[7,8]。然而, 由于所使用的发光材料含有Cd等重金属元素, 对环境和人体有一定的危害, 在商业化过程中面临很大的挑战。因此, 发展低毒无镉的半导体纳米晶并将其应用于电致发光器件具有非常重要的意义。目前, 无镉半导体纳米晶主要包括锌基II-VI族化合物、InP为代表的III-V族化合物和多元铜基硫族化合物等。锌基II-VI族化合物由于其光学带隙较宽, 其发光范围仅限于蓝紫光区域, 不能在较大范围内进行发光颜色调控, 因此

其在电致发光器件方面的应用受到了一定限制。而InP基III-V族半导体量子点合成方法较为复杂, 其合成化学远远落后于镉基硫族半导体纳米晶, 限制了其大规模的应用开发。

与传统的II-VI族半导体纳米晶相比较, 三元铜基硫族半导体纳米晶(如CuInS₂等)可认为是II-VI族化合物中的二价金属离子(如Zn²⁺等)被一价铜离子(Cu⁺)和三价铟离子(In³⁺)所取代, 因此三元CuInS₂纳米晶的晶型与II-VI族纳米晶相似^[9,10]。三元CuInS₂纳米晶的晶型主要包括闪锌矿、纤锌矿和黄铜矿三种晶型结构, 不同的晶型结构常常具有不同的光学带隙^[11,12]。大部分铜基硫族半导体纳米晶可通过胶体化学方法制备, 其合成过程中的反应参数如温度、反应前驱体活性和表面配体等对材料的尺寸、形貌和组分有着重要影响。由于大多数铜基硫族半导体纳米晶都表现出非化学计

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量比特性, 因此其铜空位的数目在某种程度上影响其发光性能^[13~15]. 为了提高三元CuInS₂纳米晶的发光性能, 研究人员通常在合成体系中引入Zn²⁺形成四元Cu-In-Zn-S合金结构, 或在其表面外延生长宽带隙半导体材料(如ZnS)形成CuInS₂/ZnS核壳结构^[16~18]. 然而, 由于Cu⁺在高温下具有较大的离子迁移率, 且Cu⁺半径和Zn²⁺相似, 在外延生长ZnS壳层时容易发生阳离子交换反应, 因此多元铜基硫族纳米晶的合金结构和核壳结构在某种程度上很难区分. 目前, 除了三元CuInS₂和四元Cu-In-Zn-S纳米晶外, 研究较多的铜基硫族半导体纳米晶还包括三元CuInSe₂、CuGaS₂和四元Cu-In-Zn-Se、Cu-Ga-Zn-S等.

随着研究人员对多元铜基硫族半导体纳米晶纳米结构和发光性能的认识, 多元铜基硫族半导体纳米晶作为发光层被广泛应用于电致发光器件^[19~22]. 目前, 研究人员通过改变器件结构、调控材料的纳米结构及器件的界面工程等策略, 有效改善了多元铜基硫族纳米晶电致发光器件的器件性能, 其黄光和红光器件的外量子产率均接近8%^[23,24]. 本综述将首先介绍多元铜基硫族半导体纳米晶的发光性能, 重点介绍材料的组分调节、表面配体、晶体结构和纳米结构等对其光学性能的影响, 然后阐述材料的纳米结构调控和界面工程调控等途径对多元铜基硫族半导体纳米晶电致发光器件的性能优化, 最后对多元铜基硫族半导体纳米晶的发展前景作出展望.

1 多元铜基硫族半导体纳米晶的发光性能

在众多多元铜基硫族半导体纳米晶中, 三元CuInS₂纳米晶的研究最为广泛. 它是一种直接带隙半导体材料, 体材料的光学带隙为1.5 eV, 其激子玻尔半径为4.1 nm, 因此, 在尺寸约8 nm的CuInS₂纳米晶中可以观察到明显的量子限域效应^[13,25]. 如图1所示, 通过改变CuInS₂纳米晶的尺寸, 可以在整个可见光区范围内调节它的吸收光谱^[26]. 与此同时, 多元铜基硫族半导体纳米晶的光学带隙还可以通过改变化学组分进行调节, 即通过改变多元铜基硫族半导体纳米晶中所含不同元素的比例, 就可以调节其吸收和光致发光的范围^[14]. 除此之外, 多元铜基硫族半导体纳米晶还常常具有较大的斯托克斯位移和较高的光致发光量子产率^[27,28]. 但是, 高温下铜离子具有较大的离子迁移率, 使得多元铜基硫族半导体纳米晶不仅存在表面缺陷还存在内部缺陷, 因此其发光机理与传统的II-VI族半导

图1 (网络版彩色)不同温度下合成的不同尺寸CuInS₂纳米晶的吸收光谱^[26]

Figure 1 (Color online) Absorption spectra of CuInS₂ nanocrystals with different sizes synthesized at different temperatures^[26]

体纳米晶有很大的不同. 目前, 对于三元和四元铜基硫族半导体纳米晶的发光机理还没有达成共识.

1.1 多元铜基硫族半导体纳米晶的发光机理

由于多元铜基硫族半导体纳米晶具有复杂的晶体结构和非化学计量比的特性, 其发光机理也存在多种解释. 目前广泛接受的观点是铜基硫族半导体纳米晶的发光来自施主-受主对(donor-acceptor pair, DAP)复合^[29~31]. 在这种机制中, 带电载流子将从导带能级转移到施主能级, 然后再弛豫到价带或受主能级. 材料结构和组成的复杂性导致其存在多种施主能级与受主能级. CuInS₂纳米晶有一种受主能级(V_{Cu} :Cu空位)和两种施主能级(V_S :S空位, In_{Cu} :In替代Cu), 当纳米晶的光学带隙变大时, 施主能级和受主能级也会分别向导带和价带方向移动^[32]. 但是, 引起CuInS₂纳米晶发光的DAP复合类型还不统一. 例如, Nam等人^[33]认为, CuInS₂纳米晶的DAP复合来自 V_S - V_{Cu} (图2), 而不是 In_{Cu} - V_{Cu} , 因为 In_{Cu} - V_{Cu} 的复合会产生近红外发射. 而Omata等人^[34]通过有限深势阱的有效质量近似计算与实验结果的对比, 认为主要复合路径来自低于导带~0.1 eV的施主能级与受主能级, V_S 缺陷与 In_{Cu} 缺陷作为施主能级都与计算结果相符合. 在CuInS₂纳米晶表面上外延生长ZnS壳层后, 纳米晶表面和内部空位大幅度减少, V_S 与 V_{Cu} 数量明显降低, 此时主要复合途径变为导带与 V_{Cu} 之间的复合(图2), 从而其光学带隙变宽, 发射峰蓝移. 最近, 也有一些研究结果从更深层次揭示了多元铜基硫族半导体纳米晶的发光机理. 例如, Jara等人^[35]观察和研究了两种不同的转变, 他们将高能跃迁定义为带边跃迁, 将低能跃迁定义为亚带隙跃迁, 并将这两个跃迁分配给 τ_1 , τ_2 (发

图3 (网络版彩色)不同Cu/In前驱体比例下制备的Cu-In-Zn-S纳米晶的光学表征^[40]。(a) 紫外-可见吸收光谱; (b) 光致发光光谱; (c) 样品溶液在紫外灯照射前后的数码照片

Figure 3 (Color online) Optical characterization of Cu-In-Zn-S nanocrystals prepared with different Cu/In precursor ratios^[40]. (a) The UV-Vis absorption spectra; (b) photoluminescence (PL) spectra; (c) digital pictures of the corresponding products before and after illumination under UV light

图4 (网络版彩色)不同Cu前驱体用量下所制备的Cu-In-Zn-Se-S纳米晶的光谱和结构表征结果^[20]。(a) 吸收光谱和PL光谱; (b) XRD图谱; (c) 光致发光量子产率; (d) 紫外灯照射下的图片

Figure 4 (Color online) Optical and structural characterization of Cu-In-Zn-Se-S nanocrystals synthesized by using different Cu precursors dosage^[20]. (a) The absorption and PL spectra; (b) XRD (X-ray diffraction) patterns; (c) PL quantum yields (PLQY); (d) digital pictures under UV light irradiation

羧酸, 通常能有效地保证纳米颗粒在有机溶剂中稳定存在。合成三元CuInS₂纳米晶常用的表面配体包括有机胺、硫醇、羧酸、有机膦或膦酸等。为了平衡反应过程中不同阳离子的反应活性且满足纳米晶的多功能应用需求, 在CuInS₂纳米晶的合成中通常会发生配体交换, 转换为功能性配体或几种不同配体的混合物^[22,42,43], 因此CuInS₂纳米晶的表面可能会被几种不同配体所包覆^[44-46]。但是, 表面配体的多样性增加了对纳

米晶组成和结构控制的复杂性, 阻碍了半导体纳米晶的大规模合成。因此, 近年来也有使用单配体合成CuInS₂纳米晶的报道^[47,23]。另外, CuInS₂纳米晶的一些关键因素如有机配体的分子结构、无机配体的杂质缺陷等会阻碍电荷的转移^[48]。因此, CuInS₂纳米晶表面配体的种类不仅影响纳米晶的表面性质, 而且还影响其发光性能^[49]。

DDT是合成多元铜基硫族半导体纳米晶常用的表

面配体, DDT的C-S键在高温下断裂还可以提供硫源. 以DDT为表面配体的合成方法简单有效, 且合成的多元铜基硫族半导体纳米晶的光致发光量子产率较高, 所以目前DDT是普遍使用的表面配体^[47]. 而非配位性表面活性剂ODE也是广泛使用的有机溶剂, 但ODE与DDT在高温下会发生反应生成十二烷基硫醚^[50], 引入额外的杂质, 加大洗涤难度. 为了克服这一问题, 吉林大学杨柏教授课题组^[23]以DDT作为单一溶剂、单一配体合成了Cu-In-S/ZnS核壳结构纳米晶. 仅使用DDT作为配体和溶剂不仅减少了副产物的生成, 而且避免了不同种类配体之间的质子转移, 提高了无机半导体纳米晶的胶体稳定性. 进一步地, 他们还通过控制阳离子的摩尔投料比, 改善了纳米晶薄膜的电学性能, 使其表面化学性质得到优化.

一般情况下, 使用热注射法、直接加热法和溶剂热法等有机溶剂中合成的胶体半导体纳米晶表面是疏水性的, 而当纳米晶应用于生物标记时, 为了提高纳米晶的相容性, 通常要求其表面是亲水性的^[51,52], 因此人们开发了一系列表面改性的方法. 目前常用的改性方法有配体交换法^[53,54]、表面硅烷化法^[55]、两亲分子封装法^[56,57]等. 其中, 配体交换法因其操作简单、水合半径小等优点而受到越来越多的关注. 然而, 通常经过配体交换得到的亲水性半导体纳米晶的光致发光量子产率较之前有明显的降低^[58]. 使用具有强键合能力的配体合成的半导体纳米晶容易产生高的光致发光量子产率, 但也难以发生配体交换, 因为这个交换过程需要

更多的能量^[58]. 硫醇作为配体, 与多元铜基硫族纳米晶的表面具有强结合力, 导致配体交换过程很难进行^[59]. 但是, 硫醇作为表面配体得到的半导体纳米晶往往具有较高的量子产率. 为解决这一难题, 韩国学者Jeon课题组^[60]通过调控所使用的硫醇和有机氨类两种配体的比例, 既提高了半导体纳米晶的光致发光量子产率, 又实现了配体交换的可操作性. 如图5所示, 在ZnS壳层生长过程中同时加入DDT和OM或十二胺(DDA), 通过控制配体的使用比例来控制所生成的CuInS₂/ZnS核壳纳米晶表面配体的比例, 所得到的纳米晶的发光量子产率可达到仅使用DDT作为表面配体时纳米晶的90%, 同时还保持了良好的配体交换性.

1.4 晶体结构对铜基硫族半导体纳米晶发光性能的影响

体相CuInS₂在室温时呈黄铜矿结构, 而闪锌矿和纤锌矿结构的CuInS₂只有在高温下才能稳定存在. 与之形成鲜明对比的是, 闪锌矿和纤锌矿结构的CuInS₂纳米晶在室温下也能稳定存在. 黄铜矿结构的CuInS₂是最常见的, 室温下其金属原子有序地排列在阳离子亚晶格中. 然而, 在闪锌矿和纤锌矿结构的CuInS₂中, 金属原子随机分布在阳离子亚晶格中. 因此, 与黄铜矿结构相比, 闪锌矿和纤锌矿结构在化学计量上具有更大的灵活性^[61]. 有报道指出, 不同晶体结构的CuInS₂纳米晶具有不同的光学带隙^[62]. 目前, 已有多个研究小组报道了不同晶体结构的CuInS₂纳米晶的选择性合成及

图5 (网络版彩色)配体交换的过程以及光致发光量子产率的变化^[60]

Figure 5 (Color online) The process of ligand exchange and the change of PLQY^[60]

晶体结构对CuInS₂纳米晶光学性能的影响^[63-68].

CuInS₂纳米晶的晶体结构可以通过调控表面配体、硫源和溶剂的类型等条件进行改变^[67,69,70]. 例如, 可以通过改变表面配体与金属前驱体的配位强度调控晶型, 当金属前驱体与DDT在ODE或油酸中加热时, 可得到闪锌矿结构的CuInS₂纳米晶. 而当金属前驱体与DDT在OM或三正辛基氧磷(TOPO)中加热时, 则可得到纤锌矿型CuInS₂纳米晶^[70]. 也就是说, 采用非配位性溶剂或弱配位溶剂时可得到闪锌矿结构, 而采用强配位溶剂则有利于合成纤锌矿结构. 研究表明, 不同晶体结构的CuInS₂纳米晶形成过程中, 关键的一步是反应中间体CuIn(SR)_x的稳定性和结晶度. 结晶度高的中间体会产生纤锌矿结构的CuInS₂纳米晶, 而结晶度低的中间体会转变为闪锌矿结构的CuInS₂纳米晶. Batabyal等人^[67]通过控制反应温度及表面配体的比例, 实现了不同晶体结构CuInS₂纳米晶的合成, 在DDT或TOPO存在下, 通过改变单源金属前驱体热分解的反应温度来控制CuInS₂纳米晶的晶体结构. 例如, 在前驱体与表面配体TOPO和DDT的比例为1:50:50下, 反应温度低于250°C时生成纤锌矿结构, 高于250°C时则得到闪锌矿结构, 且在300°C时可以得到闪锌矿结构的纯相. 但当TOPO的用量增加后, 即使在300°C时也可以得到稳定的纤锌矿结构. 纤锌矿和闪锌矿结构CuInS₂纳米晶的吸收带很宽, 吸收尾部在800 nm左右, 说明这两种晶体结构的CuInS₂纳米晶适合应用在太阳能电池中, 且闪锌矿结构的CuInS₂纳米晶具有较高的双光子吸收截面, 可应用于超快光敏处理和光学限幅等光学器件中. 除此之外, 我们课题组研究了金属前驱体中阴离子类型及金属前驱体的摩尔比对CuInS₂纳米晶晶体结构的影响^[68].

当分别选择Cu(acac)₂, CuCl, Cu(NO₃)₂为铜源, In(acac)₃, InCl₃和In(NO₃)₃作为铟源时, 通过调控反应温度可得到闪锌矿、纤锌矿、黄铜矿、纤锌矿-闪锌矿混合结构的CuInS₂纳米晶(图6(a)), 这些不同晶体结构的CuInS₂纳米晶具有不同的光学吸收特性(图6(b)).

不同晶体结构的CuInS₂纳米晶不仅在吸收光谱上表现出明显的差异, 而且其光致发光光谱也有所不同^[71]. 如图6(c)所示, 这三种不同晶体结构的CuInS₂纳米晶在可见光到近红外光区域都表现出较强的吸收, 尤其是黄铜矿结构纳米晶的吸收强度尤为显著, 明显高出其他晶体结构. 从光致发光光谱中可以观察到, 每种晶体结构的发光峰位置都在1.40~1.62 eV之间, 但不同晶体结构之间差异较明显, 黄铜矿结构在752 nm (1.59 eV)处具有很强的光致发光峰, 而闪锌矿结构在739 nm (1.62 eV)处具有较强的光致发光峰, 纤锌矿结构在755 nm (1.58 eV)处有光致发光峰, 发光峰位置有轻微移动.

1.5 纳米结构对铜基硫族半导体纳米晶发光性能的影响

半导体纳米晶的纳米结构对其发光性能有着非常重要的影响. 例如, 由于半导体纳米晶的尺寸较小, 其具有很大的比表面积, 因此在其表面存在大量的不饱和键和表面缺陷态, 使得没有包覆的半导体纳米晶发光性能受到影响, 需要有效的表面钝化来消除表面缺陷态优化其发光性能. 在三元铜基硫族纳米晶体系中引入Zn²⁺或包覆宽禁带的ZnS壳层是消除表面缺陷态最常用的方法之一. Zn²⁺的引入可占据纳米晶晶格中Cu(I)和/或In(III)的位置形成四元合金结构, 从而提高

图6 (网络版彩色)不同晶体结构CuInS₂纳米晶的形貌与光学性能表征结果. (a) 阴离子对CuInS₂纳米晶晶相和形貌的影响^[68]; (b) 不同晶相CuInS₂纳米晶的吸收光谱^[68]; (c) 不同晶相CuInS₂纳米晶的紫外-可见-近红外光谱和荧光光谱^[71]

Figure 6 (Color online) Morphology and optical characterization of CuInS₂ nanocrystals with different crystal structures. (a) The effect of anions on phase and morphology of CuInS₂ nanocrystals^[68]; (b) the absorption spectra of CuInS₂ nanocrystals in different crystal phases^[68]; (c) UV-Vis-NIR and PL spectra of CuInS₂ nanocrystals in different crystal phases^[71]

发光强度^[21,40,72,73]。我们课题组在CuInS₂纳米晶的合成体系中引入Zn²⁺得到了四元Cu-In-Zn-S纳米晶,随着Zn²⁺的进入,吸收带边和光致发光峰位置较CuInS₂纳米晶有明显的蓝移,而且发光强度明显提高^[40]。为了进一步提高其发光性能,通常采用在其表面外延生长无机壳层。一般来说,半导体纳米晶的壳层材料可以根据不同的需求进行选择,根据核芯材料和壳层材料导带和价带的位置可以将核壳结构材料分为不同类型。其中,I型核壳结构是将较宽带隙的材料包覆在窄带隙的核芯材料上,核芯材料的导带比壳层材料低,而价带比壳层材料高,使得空穴和电子都被限制在核芯内,减少了非辐射复合,提升了光致发光效率和化学稳定性。由于ZnS的光学带隙较宽(3.7 eV),且闪锌矿结构的ZnS与黄铜矿结构的三元Cu-In-S纳米晶的晶格失配度小,是多元铜基硫族半导体纳米晶常用的壳层材料^[74-76]。目前,国内外许多课题组采用不同的胶体化学方法在三元CuInS₂和四元Cu-Zn-In-S纳米晶的表面外延生长了ZnS壳层,其光致发光效率有了大幅提高,光致发光峰位置较没有包覆前发生了明显蓝移。这与传统CdSe纳米晶表面包覆ZnS壳层后光致发光峰发生红移的现象正好相反^[77-79]。对于这一反常现象,目前国内外不同课题组提出了几种不同的解释,如阳离子的相互扩散^[80]、CuInS₂核芯材料的刻蚀^[74]和纳米晶的表面重构^[46]。在这些解释中,阳离子扩散得到了广泛认可。韩国Park课题组^[81]使用不同的Zn前驱体合成了CuInS₂/ZnS纳米晶,包覆ZnS壳层后,光致发光光谱出现了蓝移现象。研究发现,Cu⁺、In³⁺与Zn²⁺在CuInS₂纳米晶的表面发生了阳离子交换,使得核芯尺寸减小,引起了光致发光光谱的蓝移。实际上,由于Cu⁺在高温下具有较大的离子迁移率,且Cu⁺离子半径与Zn²⁺很相似,因此,在壳层生长过程中很容易发生阳离子交换生成合金结构。Zn²⁺的引入和ZnS壳层的生长是有竞争的,如何平衡这两个过程对控制多元铜基硫族半导体纳米晶的纳米结构有着非常重要的影响。最近,我们课题组通过控制Zn前驱体的用量和注射速度来平衡Zn²⁺扩散与ZnS壳层生长这两个过程,从而实现对Cu-In-Zn-S纳米结构的调控^[82]。制备Cu-In-Zn-S纳米晶时,如果Zn前驱体的用量较大,Zn²⁺主要集中在核芯Cu-In-Zn-S纳米晶的表面。随着反应时间的延长,Zn²⁺不断进入晶格中,而部分Cu⁺扩散到外面,使得光谱发生蓝移。当Zn前驱体用量较少时,随着时间延长,光谱发生红移。因此,如果在核生长阶段,随着反应温度的升高,将Zn前驱体分多次缓慢地逐滴注射,可以使

Zn²⁺充分扩散到纳米晶中。当反应达到最高温度时,再快速单次注射大量的Zn前驱体,就可以形成ZnS壳层。通过精细调控前驱体用量和注射速度,有效控制了梯度分布的纳米结构,有效减少了纳米晶内部和表面缺陷,使得样品的光致发光量子产率达到了90%,实现了发光寿命单指数衰减的规律(图7)。此外,将该纳米晶与蓝光LED芯片组合,制作了白光LED器件,该器件的CIE坐标为(0.33,0.33),器件效率达到了60.2 lm/W。

2 多元铜基硫族半导体纳米晶在电致发光器件中的应用

半导体纳米晶由于其色纯度高、色域广及稳定性好等优势在下一代显示和照明方面有着潜在的应用。在电致发光器件中,电子和空穴分别从阴阳两极通过载流子注入层和传输层注入到半导体纳米晶发光层中复合形成激子而通过辐射复合发光。目前,基于传统镉基半导体纳米晶红绿蓝三基色电致发光器件的外量子效率均超过了20%,其稳定性也有了重大突破。然而,随着国际社会对电子器件中禁止使用Cd达成共识,开发低毒无镉半导体纳米晶电致发光器件引起了广大科研工作者的关注。近年来,除了InP基半导体纳米晶电致发光器件取得了突破性进展,基于多元铜基硫族半导体纳米晶的电致发光器件也得到了快速发展^[83-93]。下面将从多元铜基硫族半导体纳米晶的组分和结构优化、器件结构调控及界面工程等方面优化电致发光器件性能进行介绍。

2.1 发光层的组分、结构和表面配体调控

2011年,Tan等人^[83]率先使用具有CuInS₂-ZnS合金核芯和ZnSe/ZnS双壳层的核壳结构纳米晶作为发光层,构筑了结构为ITO/PEDOT:PSS/Poly-TPD/纳米晶/Alq₃/Ca/Al的红黄绿三色电致发光器件,虽然器件的电流效率小于1 cd A⁻¹,但该工作给多元铜基硫族半导体纳米晶在电致发光器件中应用提供了依据。在此基础上,华东理工大学钟新华课题组^[22]使用发光量子产率高达85%的多元铜基硫族纳米晶作为发光层构筑了电致发光器件,其效率最高达2.45 cd A⁻¹。近年来,我们课题组采用红黄绿三色Cu-In-Zn-S/ZnS纳米晶作为发光层,采用全溶液处理手段构筑了启亮电压小于2 V的电致发光器件,红黄绿三色电致发光器件的峰值电流效率分别为1.16、7.71和0.84 cd A⁻¹,对应的峰值外量子效率分别为0.91%、2.42%和0.25%^[90]。为了提高器件效率,

图7 (网络版彩色)通过控制Zn前驱体用量和注射速度得到的Cu-In-Zn-S纳米晶的光学结果^[82]。(a) 两步注射法得到的Cu-In-Zn-S纳米晶的PL光谱随反应过程的变化;(b) Cu-In-Zn-S纳米晶粉末(最终产物)在紫外灯(365 nm)照射前后的图片(左),以及在聚二甲基硅氧烷(PDMS)基质中稀释的Cu-In-Zn-S纳米晶(0.1wt%)在紫外灯(365 nm)照射前后的图片(右);(c) 最终产物的PL衰减曲线;(d) 蓝光LED芯片和所制备的白光LED的发射光谱,插图显示了白光LED在施加驱动电压前后的图像

Figure 7 (Color online) Optical spectra of Cu-In-Zn-S nanocrystals obtained by controlling the amount of Zn precursor and the injection speed^[82]. (a) PL spectra evolution of Cu-In-Zn-S nanocrystals obtained by two-step injection method with the reaction process. (b) Digital pictures: (left) Final product's powder before and after being excited by the UV light (365 nm); (right) 0.1wt% of final product in PDMS column before and after being excited by the UV light (365 nm). (c) The PL decay curve of the final product. (d) The emission spectra of a blue LED chip and the as-prepared white LEDs, the inset shows the digital pictures of the white LED before and after applying the driving voltage

Yang课题组^[24]通过延长纳米晶壳层的生长时间,并在壳层生长过程中不断补充前驱体来调节壳层厚度及核/壳界面处的合金化程度,最终得到尺寸为3.8~7.1 nm的Cu-In-S/ZnS核壳结构纳米晶。这种结构的纳米晶能够有效抑制俄歇复合和Förster共振能量转移的发生,从而提高辐射复合的效率。以该纳米晶作为发光层构筑了电致发光器件,该器件的最大亮度、电流效率和外量子效率分别为 8464 cd m^{-2} 、 18.2 cd A^{-1} 、7.3%。纳米晶的结构和器件性能如图8所示。为了提高红色电致发光器件的器件性能,最近我们课题组采用Se元素取代部分S元素,并通过调节Cu和Se元素的含量,使材料的光致发光峰在610~665 nm之间进行调节。以该材料作为发光层构筑了器件结构如ITO/PEDOT:PSS/TFB/纳米晶/Cl@ZnO:Mg/Al的电致发光器件,器件的最大外量子效率达到4.2%(图9)^[20]。除了引入阴离子,改变阳离子也能改变多元铜基硫族纳米晶的发光波长, Yang课题组通过在Cu-In-S/ZnS纳米晶中引入 Ga^{3+} 调控发光峰的位置从

605 nm蓝移至474 nm处,使得光致发光量子产率高达80%,基于该纳米晶的电致发光器件峰值外量子效率和电流效率分别高达7.1%和 11.8 cd A^{-1} 。在此基础上,该课题组把该纳米晶与黄色Cu-In-S/ZnS纳米晶按照一定比例混合制备了白光LEDs,器件的显色指数为82,最大亮度达 2172 cd m^{-2} ,外量子效率超过4%(4.6%)^[94]。基于多元铜基硫族纳米材料的蓝光和白光电致发光器件的器件结构及性能如图10(a)所示。吉林大学杨柏教授课题组^[23]以DDT作为单一溶剂和单一配体合成了Cu-In-S/ZnS核壳结构的纳米晶,该方法不仅能够增加溶液的稳定性,还能提高纳米晶薄膜的电学性质,使相应电致发光器件的最大外量子效率达到7.8%。

除了纳米晶的组分和结构,纳米晶表面的有机配体选择也是影响器件性能的重要因素^[88,89]。若有机配体的碳链较长,虽然纳米晶具有较好的溶解性,但是有机物本身的绝缘性会影响器件中电荷的注入;若有机配体的碳链较短,则纳米晶的溶解性较差,容易发生团聚,因此

图8 (网络版彩色)厚壳层Cu-In-Zn-S/ZnS//ZnS纳米晶的合成过程示意图及电致发光器件性能^[24]

Figure 8 (Color online) Schematic of the synthesis procedure for thick shell Cu-In-Zn-S/ZnS//ZnS nanocrystals and performance of the electroluminescent devices^[24]

图9 (网络版彩色)基于Cu-In-Zn-Se-S纳米晶的电致发光器件的器件性能^[20]. (a) 电流密度-电压曲线; (b) 外量子效率-亮度曲线; (c) 器件性能统计图; (d) 功率效率-电流效率-亮度曲线; (e) 不同Cu含量纳米晶的电致发光光谱图

Figure 9 (Color online) Device performance of the electroluminescent devices based on Cu-In-Zn-Se-S nanocrystals^[20]. (a) Current density-voltage curves; (b) external quantum efficiency-luminance curve; (c) statistical diagram of efficiency; (d) power efficiency-current efficiency-luminance curve; (e) electroluminescent spectra of the devices based on different samples with different Cu concentrations

合适配体的选择十分重要. 2016年, 北京理工大学钟海政课题组^[88]探讨了纳米晶表面配体对倒置结构电致发光器件性能的影响. 他们采用原位配体交换的方法, 用6-巯基己醇替换了原来的长链配体OM, 不仅提高了多元铜基硫族纳米晶的电子迁移率, 还促进了电子从电子传输层向发光层的有效注入, 使器件的电流效率和外量子效率提升到 9.43 cd A^{-1} 和3.22%(图10(b)).

2.2 器件结构和界面工程调控

与有机电致发光器件结构相似, 最早的半导体纳米晶电致发光器件的结构一般包括阴极、发光层和阳极. 当器件两极施加正向偏压后, 从阴阳两极注入的电子和空穴在发光层中形成激子, 激子发生辐射复合而发光. 因此, 为了得到高效电致发光器件, 电子和空穴必须有效地注入到发光层中. 为了有效降低载流子的

图 10 (网络版彩色)基于多元铜基纳米材料的电致发光器件性能表征结果。(a) 蓝光和白光器件的结构及器件性能示意图^[94]; (b) 配体交换前后 Cu-In-S/ZnS 纳米晶示意图及器件性能曲线^[88]

Figure 10 (Color online) Device performance of the electroluminescent devices based on multinary copper-based nanomaterials. (a) Schematic diagram of structure and performance of blue and white devices^[94]; (b) schematic diagram of Cu-In-S/ZnS nanocrystals and device performance before and after ligand exchange^[88]

注入势垒,通常会引入载流子传输层,载流子传输层的存在会使电子和空穴能够更加有效地注入到发光层中。迄今较为流行的纳米晶聚合物电致发光器件是采用有机材料作为空穴传输层,而采用金属氧化物纳米晶作为电子传输层。空穴传输层的最高占据分子轨道(highest occupied molecular orbital, HOMO)能级位于阳极功函数和纳米晶的价带之间,形成阶梯型注入势垒,能够促进空穴的有效注入。另一方面,由于空穴传输层的最低未占据分子轨道(lowest unoccupied molecular orbital, LUMO)能级与纳米晶的导带之间存在较大的势垒,能够阻挡电场作用下电子向阳极的移动。同样,阴极和发光层之间的电子传输层也可促进电子的有效注入,同时阻挡空穴向阴极移动,从而把电子和空穴限制在发光层中,增加激子辐射复合的可能性。因此,基于半导体纳米晶的电致发光器件性能一方面取决于纳米晶发光层的光学性能,如前文所述,这主要通过调控纳米晶的纳米结构和组分以及尺寸和表面配体等途径解决;而另一方面取决于器件中载流子注入、传输和复合等

过程的影响,常见的调控手段包括电子传输层的修饰、界面调控及器件结构调控^[88,94-98]。

常见的研究方法包括空穴传输层(hole transport layer, HTL)的选择、量子点发光层和电子传输层(electron transfer layer, ETL)的厚度调节、ZnO作为电子传输层的元素掺杂及表面优化、倒置结构器件的构筑等。例如, Yang课题组^[85]以光致发光量子产率为65%的黄光多元铜基硫族纳米晶作为发光层,使用全溶液工艺构筑正型结构的电致发光器件,通过调控器件中电子传输层的厚度来优化器件性能。为了提高器件的亮度和效率,电子传输层的厚度在12~40 nm变化。当电子传输层的厚度约为20 nm时,器件性能达到最佳。为了进一步研究电子传输层类型对器件性能的影响,他们分别以ZnO、Zn_{0.95}Mg_{0.05}O和Zn_{0.9}Mg_{0.1}O作为电子传输层,发现使用合金结构的ZnMgO纳米颗粒作为电子传输层时,器件的峰值亮度和电流效率分别从1766 cd m⁻²和3.43 cd A⁻¹提升到2785 cd m⁻²和5.75 cd A⁻¹^[86],器件性能的提升归因于Mg²⁺的引入可使ZnO导带能级升高,

降低了发光层与电子传输层之间的能级势垒,减少了阴极和电子传输层之间的电荷积累,减少了俄歇复合的概率.胶体ZnO纳米颗粒作为电子传输层的电子迁移率高于空穴迁移率,会造成电荷在电子传输层和纳米晶发光层界面处的电荷积累.为了减少这一现象,提高载流子的输运平衡,吉林大学纪文宇课题组^[93]使用PEIE修饰的ZnO纳米颗粒作为电子传输层,构筑了高性能CuInS₂/ZnS纳米晶电致发光器件.研究发现,PEIE的引入可以平衡载流子的注入,降低ZnO/发光层界面处的电荷积累.并且,PEIE层的存在可以为电子的注入提供一个屏障,将电子限制在发光层,从而提高空穴和电子的复合率,抑制发光猝灭,该器件的峰值外量子效率达到4.8%.另一方面,胶体ZnO纳米颗粒表面存在较多的缺陷,会减少载流子在发光层的辐射复合.为了减少ZnO纳米颗粒的表面缺陷态,我们课题组在之前全溶液法制备的红黄绿三色多元铜基电致发光器件的基础之上,通过对电子传输层的修饰提升了黄色电致发光器件的性能.我们在Mg掺杂ZnO纳米颗粒的基础之上,利用Cl⁻钝化其表面得到了Cl@ZnO:Mg纳米颗粒,这种结构的纳米颗粒减少了ZnO的表面缺陷态.以黄色Cu-In-Zn-S/ZnS纳米晶作为发光层,以Cl@ZnO:Mg纳米颗粒作为电子传输层,采用全溶液方法构筑了电致发光器件,经过Cl⁻离子浓度的优化,器件的峰值外量子效率为4.05%,电流效率为12.17 cd A⁻¹(图11(a))^[91].进一步的研究发现,Mg²⁺掺杂能够促进电子从电子传输层到发光层的注入,同时降低电子迁移率,而Cl⁻钝化可减少表面缺陷态,使得载流子的注入和输运得到平衡.除了电子传输层的界面工程,空穴传输层的界面工程

也能够有效改善电致发光器件的器件性能.针对全溶液处理的红黄绿三色电致发光器件中使用的空穴传输层TFB注入势垒较大的问题,我们以黄色Cu-In-Zn-S/ZnS纳米晶作为发光层,通过引入TPD构筑双层TFB/TPD空穴传输层,形成了阶梯型空穴注入势垒,同时TPD的引入还能够抑制TFB对纳米晶发光的猝灭作用.通过对TPD厚度以及退火温度的调节,器件的最大 η_{EQE} 和电流效率分别达到5.61%和13.1 cd/A(图11(b))^[95].

虽然传统正型结构的多元铜基纳米晶电致发光器件的器件性能在过去几年取得了快速发展,但是由于倒置结构电致发光器件更容易与低成本的n型金属氧化物或非晶硅薄膜晶体管进行集成,在一些大面积高端显示器件方面有着较好的应用前景.倒置结构的电致发光器件通常采用反射阴极作为底电极,半透明金属作为顶电极,可实现顶发射.另一方面,倒置结构的电致发光器件可以避免传统正型结构器件中纳米晶发光层与下层空穴传输层或空穴注入层混合导致的荧光猝灭^[96-98].2016年,北京理工大学钟海政课题组^[88]制备了基于黄色Cu-In-S/ZnS纳米晶的倒置电致发光器件,该器件以CBP和TCTA作为空穴传输层,以热蒸镀方法制备的氧化钼(MoO₃)薄膜作为空穴注入层,以ZnO纳米颗粒作为电子传输层,结果该器件的亮度达到8375 cd m⁻²,外量子效率达到3.22%.吉林大学杨柏教授课题组^[23]以红色Cu-In-S/ZnS纳米晶作为发光层构筑了倒置电致发光器件,器件的最高外量子效率达到7.8%.吉林大学纪文宇课题组^[93]选用PEIE修饰的ZnO纳米颗粒作为电子传输层,CBP作为空穴传输层,MoO₃作为空穴注入层,红色Cu-In-S/ZnS纳米晶作为发光层,构筑了倒置

图11 (网络版彩色)不同电子传输层和空穴传输层类型对电致发光器件性能的影响。(a)不同类型的ZnO纳米颗粒作为电子传输层,构筑的Cu-In-Zn-S基黄光电致发光器件的电流效率和外量子效率^[91];(b)具有双空穴传输层的Cu-In-Zn-S/ZnS纳米晶电致发光器件的结构与性能示意图^[95]
Figure 11 (Color online) The effects of different electron transport layers and hole transport layers on the device performance of the electroluminescent devices. (a) Current efficiency and external quantum efficiency of yellow-colored Cu-In-Zn-S-based devices constructed with different types of ZnO nanoparticles (NPs) as the electron transport layers^[91]. (b) The schematic diagram of structure and device performance of Cu-In-Zn-S/ZnS electroluminescent devices with double-layered hole transport layers^[95]

结构的电致发光器件,器件的电流效率达到 2.75 cd A^{-1} . PEIE的引入对限制ZnO与发光层之间的电子传输和抑制纳米晶的发光猝灭发挥了重要作用. 表1总结了基于Cu-In-S基纳米材料作为发光层的不同颜色电致发光器件的研究进展.

考虑到多元铜基硫族半导体纳米晶较宽的光致发光光谱特性,我们课题组还探索了其在照明中的应用. 由于空穴传输层TFB也可以发射蓝光,我们在上述器件结构的基础之上,将TFB引入黄光Cu-In-Zn-S/ZnS纳米晶中,将其混合作为发光层构筑了传统结构的电致发光器件. 通过控制发光层退火温度有效调控TFB和纳米晶之间的能量传递,在较低电压下(约为 2.5 V)得到了纯白光,该白光器件的显色指数(color render index, CRI)为90, CIE坐标为(0.33, 0.32),最大亮度约为 1500 cd m^{-2} ,可以在 $100\sim 1300\text{ cd m}^{-2}$ 的高亮度范围内保持超过 0.1 cd A^{-1} 的电流效率^[99].

3 结论与展望

多元铜基硫族半导体纳米晶由于其低毒性和组分调控的发光特性在电致发光器件应用方面展现出巨大潜力,成为下一代照明和显示的有力竞争者之一. 本文围绕多元铜基硫族半导体纳米晶的光学特性调控及其在电致发光器件中的应用展开综述. 一方面,阐述了多元铜基硫族半导体纳米晶的组分、表面配体、晶体结构和纳米结构等因素对其发光特性的影响;另一方面,讨论了多元铜基硫族半导体纳米晶的纳米结构和表面配体及器件结构和界面工程等对多元铜基硫族纳米晶电致发光器件的器件性能影响. 经过广大科学工作者的努力,从材料性能的优化到器件结构、界面工程等方面的协同作用,基于多元铜基硫族半导体纳米晶的电致发光器件性能有了较大提高,然而器件性能与传统的铜基硫族半导体纳米晶相比较还有很大提升空间.

表 1 基于多元铜基硫族半导体纳米晶的电致发光器件性能总结

Table 1 Summary of the device performance of the electroluminescent devices based on different types of multinary copper chalcogenide nanocrystals

年份	器件结构	器件类型	发光峰位 (nm)	外量子效率 (%)	电流效率 (cd A^{-1})	峰值亮度 (cd m^{-2})	文献
			622	—	0.58	1200	
2011	ITO/PEDOT:PSS/Poly-TPD/ZCIS/ZnSe/ZnS/Alq ₃ /Ca/Al	正型	580	—	0.49	1160	[83]
			553	—	0.62	1600	
2011	ITO/Poly-TPD/CuInSe ₂ /ZnS/TPBi/LiF/Al	正型	682	>0.3%	—	30	[84]
2012	ITO/Poly-TPD/CIS/ZnSeS/ZnS/Alq ₃ /Ca/Al	正型	606	—	0.92	1700	
			577	—	0.88	2100	[21]
2014	ITO/PEDOT:PSS/Poly-TPD/ZCIS/ZnS/TPBi/LiF/Al	正型	580	—	2.45	220	[22]
2014	ITO/PEDOT:PSS/PVK/CIS/ZnS(Thickness)/ZnO/Al	正型	580	2.52	1.1	1564	[85]
			579	2.19	5.75	2785	
2015	ITO/PEDOT:PSS/PVK/CIS/ZnS/ZnMgO/Al	正型	562	0.99	2.75	1564	[86]
			541	0.51	1.5	1009	
2016	ITO/ZnO/CIS/ZnS-MCH/CBP/TCTA/MoO ₃ /Al	倒置	560	3.22	9.43	8375	[88]
			642	0.91	1.16	1247	
2016	ITO/PEDOT:PSS/TFB/CIS/ZnS/ZnO/Al	正型	552	2.42	7.71	3061	[90]
			540	0.25	0.84	1100	
2016	ITO/PEDOT:PSS/TFB/CIS/ZnS/ZnO/Al	正型	577	7.3	18.2	8464	[24]
2018	ITO/ZnO/CIS/ZnS-DDT/TCTA/MoO ₃ /Al	倒置	635	7.8	8.3	4490	[23]
2018	ITO/PEDOT:PSS/TFB/CIZSeS/ZnS/ZnO/Al	正型	664	—	0.4	1502	[19]
2018	ITO/PEDOT:PSS/TFB/CIZS/ZnS/Cl@ZnO:Mg/Al	正型	557	4.05	12.17	3185	[91]
2019	ITO/ZnO/CIS/ZnS/HTL/MoO ₃ /Al	倒置	627	—	2.03	2861	[92]
2019	ITO/PEDOT:PSS/TFB/CIZSeS/ZnS/Cl@ZnO:Mg/Al	正型	665	4.2	0.76	≈1000	[20]
2019	ITO/ZnO/PEIE/CuInS ₂ /ZnS QDs/CBP/MoO ₃ /Al	倒置	627	4.8	2.75	2227	[93]
2019	ITO /PEDOT:PSS/PVK/CGZS/ZnMgO/Al	正型	474	7.1	11.8	1404	[94]
2020	ITO/PEDOT:PSS/HTLs/CIZS/ZnS NCs/ZnO:Mg NPs/Al	正型	558	5.61	13.1	3257	[95]

以下三个方面对多元铜基硫族半导体纳米晶的结构优化和电致发光器件的器件性能提升有一定的指导意义。

(1) 多元铜基硫族半导体纳米晶的结构控制和发光光谱窄化。由于高温下铜离子的高迁移率, 壳层的外延生长和阳离子扩散两个过程的竞争对纳米结构的控制有一定的难度, 如何寻求一种方法控制纳米结构, 对多元铜基硫族纳米晶的光学性能和电学性能有着非常重要的意义。另一方面, 多元铜基硫族半导体纳米晶的发光光谱较宽, 如何窄化其发光光谱对其在显示方面的应用潜力有决定性作用。

(2) 基于多元铜基硫族半导体纳米晶的电致发光器件性能还有较大的提升空间。进一步发展与该类材

料体系匹配的器件结构, 寻求能够有效平衡载流子注入和输运的电荷传输材料, 对提升器件结构有着至关重要的作用。同时, 如何发展基于多元铜基硫族半导体纳米晶的蓝光电致发光器件也是极具挑战性的。着眼于下一步的商业化, 对喷墨打印等工艺的深入研究也是器件发展的一个重要方向。

(3) 多元铜基硫族半导体纳米晶发光机理还存在一定争议, 如何进一步澄清其发光机制对其下一步的应用将是非常重要的。由于多元铜基硫族半导体纳米晶的发光机理与传统的铜基硫族纳米晶有所不同, 基于该类纳米晶的电致发光器件物理机制也会有所区别, 因此器件工作机制的理论研究也是下一步的研究重点。

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Summary for “多元铜基硫族半导体纳米晶的发光性能及其在电致发光器件中的应用进展”

Optical properties of multinary copper chalcogenide semiconductor nanocrystals and their applications in electroluminescent devices

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In the past few decades, semiconductor nanocrystals (semiconductor quantum dots) have received widespread attention due to their high color purity and size-dependent optical properties as well as their potential applications in the next generation of lightening and displays. At present, most of the emitting layer materials in the quantum-dot electroluminescent devices are focused on cadmium-based chalcogenide quantum dots, but cadmium is harmful to the environment and human health, which faces great challenges in the future commercialization. Therefore, it is necessary to develop an environment-friendly, cadmium-free semiconductor quantum dot with excellent optoelectronic performance.

In recent years, multinary copper chalcogenide semiconductor nanocrystals have attracted extensive attention due to their low toxicity, tunable luminescent properties and potential applications in optoelectronic devices. Ternary copper-based chalcogenide semiconductor nanocrystals (such as CuInS_2 , etc.) can be considered as the counterparts of the II-VI compounds, in which the divalent metal ions (such as Zn^{2+} , etc.) are replaced by monovalent copper ions (Cu^+) and trivalent indium ions (In^{3+}). As a result, the crystal structure of ternary I-III-VI nanocrystals is similar to that of II-VI nanocrystals. Up to date, ternary CuInS_2 nanocrystals are the most widely studied among different multinary copper chalcogenide semiconductor nanocrystals. The crystal structure of ternary CuInS_2 nanocrystals mainly includes sphalerite, wurtzite and chalcopyrite phase, and different-phase CuInS_2 nanocrystals often have different optical band gaps.

With the development of colloidal chemical synthetic technique, most of the multinary copper chalcogenide semiconductor nanocrystals can be synthesized through a colloidal chemical method. The reaction parameters including temperature, reaction precursor activity and surface ligand in the synthesis process play an important role in the tuning of the size, morphology and composition of the resultant nanocrystals. Generally, ternary CuInS_2 nanocrystals have a low photoluminescence quantum yield due to their internal and surface defects. Since most of the multinary copper chalcogenide semiconductor nanocrystals exhibit non-stoichiometric characteristics, the number of copper vacancies also affects their luminescence performance to some extent. In order to improve the luminescence performance, it is a common strategy to introduce Zn^{2+} into the Cu-In-S system to form a quaternary Cu-In-Zn-S alloyed structure or grow a wide-band gap semiconductor material (such as ZnS) onto its surface to form a core-shell structure. However, due to higher ion mobility of copper ions at a relatively high temperature and the similar radius of Cu^+ ion and Zn^{2+} , cation exchange reaction is likely to occur in the epitaxial growth of ZnS shells. Therefore, it is difficult to distinguish the alloyed and core-shell structure for the multinary copper chalcogenide semiconductor nanocrystals.

With the in-depth understanding of the relationship between the nanostructure and luminescence properties of multinary copper chalcogenide semiconductor nanocrystals, these nanocrystals have been widely used as light-emitting layers in electroluminescent devices, and a significant progress has been made. At present, different strategies have been exploited to improve the device performance of the electroluminescent devices based on multinary copper chalcogenide semiconductor nanocrystals, such as changing the device structure, regulating the nanostructure of materials, and device interfacial engineering. This review gives a detailed summary on the relationship between the composition, surface ligands, crystal structure as well as the nanostructures and optical properties of the multinary copper chalcogenide semiconductor nanocrystals. Moreover, the progress of electroluminescence devices based on the multinary copper chalcogenide semiconductor nanocrystals is highlighted, and finally the prospect of the development of multinary copper chalcogenide semiconductor nanocrystals is concluded.

semiconductor nanocrystals, multinary copper chalcogenides, luminescent properties, electroluminescent devices

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