

Cs 掺杂 FAPbBr_3 薄膜变温光学特性及光伏器件设计

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摘要 甲脍(FA)基钙钛矿比甲胺(MA)基钙钛矿具有更高的内在稳定性,而无机Cs离子掺杂可以进一步提高钙钛矿的湿度、热和结构稳定性。通过一步反溶剂法制备了Cs掺杂的 $\text{FA}_{1-x}\text{Cs}_x\text{PbBr}_3$ ($x=0, 0.05, 0.10, 0.15$)钙钛矿薄膜,采用椭圆偏振光谱研究了材料的复介电函数并以此进行外量子效率(EQE)模拟。EQE模拟结果显示掺杂比例为0.05时,钙钛矿薄膜具有最高的功率转换效率(PCE),可达23.47%。进一步对 $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbBr}_3$ 进行变温椭圆偏振分析,发现:随着温度升高,材料带隙增大,在393 K左右,从变温复介电函数的二阶导谱中可观察到相变现象,钙钛矿材料由正交相转变为四方相。对基于 $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbBr}_3$ 的太阳能电池进行变温EQE模拟,结果表明:温度对器件的最高PCE影响不大,其效率可以稳定在23.47%左右,但是高温会导致器件近红外区的外量子效率降低,器件的整体响应带宽减小。

关键词 薄膜; Cs掺杂钙钛矿; 光学性质; 变温椭圆偏振光谱; 外量子效率模拟

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1 引言

近年来,有机-无机金属卤化物钙钛矿太阳能电池(PSCs)受到了前所未有的关注,其功率转换效率迅速提升至26.08%,已成为最具前景的第三代光伏电池材料之一^[1]。钙钛矿材料具有较大的吸收系数、较长的载流子扩散长度,以及可调节的带隙和高电荷载流子迁移率^[2-3],是理想的太阳能电池吸收层材料。但是钙钛矿材料本身在光、热和湿度下的不稳定性阻碍了其大规模的商业应用。钙钛矿材料的化学式为 ABX_3 ,由A位阳离子(MA^+ , FA^+ , Cs^+)、B位金属阳离子(Pb^{2+} , Sn^{2+} , Ge^{2+})和X位卤素阴离子(Cl^- , Br^- , I^-)构成。通过A位阳离子和X位卤素阴离子的精细调节,能够调控材料的带隙、光电特性以及晶体结构稳定性。MA基钙钛矿是最为经典的钙钛矿结构,但是,MA基钙钛矿本身的湿度稳定性差,且当环境温度升高时,MAPbX₃会分解为气态甲胺,导致PSCs快速降解^[4-5]。以 FA^+ 、 Cs^+ 或二者的组合形式替代A位中的 MA^+ 不失为一种获取高稳定性钙钛矿材料的有效途径^[6]。FA基钙钛矿比MA基钙钛矿表现出更好的热稳定性和较长的载流子寿命^[7-8]。 Cs^+ 的离子半径远小于有机基团的离子半径, Cs^+ 掺杂诱导的晶格收缩,能够有效地稳定晶体结构^[9-10],从而极大地提高钙钛矿的热稳定

性。例如,MAPbBr₃在220 °C下快速分解,而CsPbBr₃在空气中的分解温度可高达580 °C^[11]。此外,在相同的陷阱密度下, Br^- 相较于 I^- 具有更高的载流子迁移率^[12-13]。因此,选取 $\text{FA}_{1-x}\text{Cs}_x\text{PbBr}_3$ (FACsPbBr_3)(其中下标 x 为掺杂比例)薄膜为研究对象,以期获取高转换效率、高稳定性的太阳能电池。

在研究如何提升钙钛矿太阳能电池性能时,许多研究者都通过建立钙钛矿太阳能电池的光学模型并通过模拟计算外量子效率(EQE)来对器件进行优化^[14-15]。EQE模拟通过计算膜系的反射率和透射率,得到太阳能电池的外量子效率谱、短路电流密度 J_{sc} 以及电流电压曲线等,这为太阳能电池的优化提供重要依据。而在EQE模拟过程中,钙钛矿薄膜的复介电函数是重要的输入参数。此外,复介电函数与材料的能带结构和晶体结构息息相关,因此,研究Cs掺杂 $\text{FA}_{1-x}\text{Cs}_x\text{PbBr}_3$ 薄膜的复介电函数十分重要。

本文通过一步旋涂反溶剂法制备了Cs掺杂的 $\text{FA}_{1-x}\text{Cs}_x\text{PbBr}_3$ ($x=0, 0.05, 0.10, 0.15$)钙钛矿薄膜,通过椭圆偏振光谱研究了其变温光学特性。基于获取的复介电函数,根据EQE模拟光谱分析了相应太阳能电池的器件性能。结果表明, $x=0.05$ 时,Cs掺杂 FACsPbBr_3 钙钛矿材料具有最高的光电转换效率(23.47%),变温对最高转换效率的影响微弱,但会导

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致器件整体响应带宽的减小。

2 实验

2.1 样品制备

将石英衬底分别在去污剂、去离子水、乙醇、丙酮和超纯水中超声清洗 15 min, 随后用氮气枪吹干表面水分并在紫外臭氧环境下处理 15 min 以去除表面有机杂质。制备 1.4 mol/L 的 FABr 、 PbBr_2 钙钛矿前驱体溶液, 溶剂为二甲基甲酰胺 (DMF) 和二甲基亚砜 (DMSO), 体积比为 4:1, 制备 1.5 mol/L 的 CsBr 前驱体溶液, 溶剂为 DMSO。按照比例混合钙钛矿前驱体溶液, 制备 FACsPbBr_3 系列薄膜。将所需的钙钛矿前驱体溶液滴在石英衬底上, 在 6000 r/min 的转速下旋转 30 s, 高速旋转 8 s 后将一定量的氯苯快速滴加在衬底上。然后将样品放在加热板上进行阶梯退火, 先在 90 °C 条件下退火 10 min, 再在 100 °C 条件下退火 30 min, 即可制备出高质量的 Cs 掺杂 FACsPbBr_3 钙钛矿薄膜。

2.2 样品的实验测量

采用原子力显微镜表征钙钛矿系列薄膜的表面形貌特征。钙钛矿薄膜的结晶特性和物相分析采用 X 射线衍射仪 (XRD) 进行, 并运用紫外可见分光光度计分析了钙钛矿薄膜的吸收光谱。

椭圆偏振光谱是一种高度灵敏、非破坏性的光学表征技术, 基于偏振光在薄膜表面反射前后偏振态的变化, 可获取薄膜的复介电函数和厚度等参数。本文使用椭圆偏振光谱仪 (SE-VM, 武汉颐光科技) 测量并分析钙钛矿薄膜的光学性质, 测量时, 入射角为 65°, 光谱范围为 400~800 nm, 变温椭圆偏振光谱测量时, 温度的变化范围为 303~423 K, 使用 Eometrics 配套软件进行光学建模和分析。椭圆偏振光谱仪测得的椭圆参数 ψ 和 Δ 与 p 偏振光和 s 偏振光在空气和薄膜界面反射时的菲涅耳系数 R_p 和 R_s 的比值有关, 通过建立光学模型求解椭圆方程, 即可得到薄膜的厚度和复介电

函数信息, 椭圆方程的表达式^[16]为

$$\rho = \frac{R_p}{R_s} = \tan \psi \exp(i\Delta), \quad (1)$$

式中: ρ 为反射系数比。

2.3 钙钛矿太阳能电池性能模拟

通过日本岐阜大学研发的 e-ARC 软件对钙钛矿太阳能电池进行外量子效率分析和模拟。该分析软件基于光学导纳法, 建立多层膜系的特征矩阵, 可高速计算太阳能电池各膜层的反射、吸收和复合损耗, 进而得到太阳能电池的 EQE 光谱和吸收光谱。该方法充分考虑了粗糙界面引起的光散射损耗以及载流子在半导体界面和异质结部分复合引起的载流子损耗, 适用于诸如钙钛矿、硅异质结、 CuInS_2 (GIS) 等太阳能电池的优化和模拟。根据 EQE 光谱及吸收光谱, 进一步计算了 FACsPbBr_3 钙钛矿太阳能电池的短路电流密度 (J_{sc})、开路电压 (V_{oc}) 和填充因子 (F_F) 等器件参数。

3 结果与讨论

钙钛矿薄膜的形貌和器件性能之间存在着密切的关系, 如图 1(a)~(d) 所示, 反溶剂法制备的钙钛矿薄膜表面致密排布无孔洞, 呈现鹅卵石颗粒状, 是高质量的钙钛矿薄膜。原子力显微镜 (AFM) 测试结果表明 $\text{FA}_{1-x}\text{Cs}_x\text{PbBr}_3$ ($x=0, 0.05, 0.10, 0.15$) 薄膜的表面粗糙度分别为 44.1 nm、45.1 nm、48.6 nm 和 51.7 nm。图 1(e) 给出了不同 Cs 掺杂浓度的 FACsPbBr_3 钙钛矿薄膜的 XRD 图谱, 从图中可观察到两个分别位于 14.7° 和 29.9° 的强衍射峰。这两个衍射峰强度相对较高, 无劈裂, 再次说明钙钛矿薄膜具有择优取向, 表现出良好的结晶性, 薄膜具有较高的质量。而当 x 为 0.10 和 0.15 时, 在 12.3° 和 31.2° 附近检测到两个强度微弱的衍射峰。这表明此时钙钛矿薄膜出现明显的非钙钛矿 δ 相。过多的 Cs^+ 掺杂诱导晶格畸变, 导致非钙钛矿 δ 相的出现, 而 δ 相往往使得 PSCs 性能降低^[17], 这与文章后续的 PSCs 器件性能模拟结果相一致。

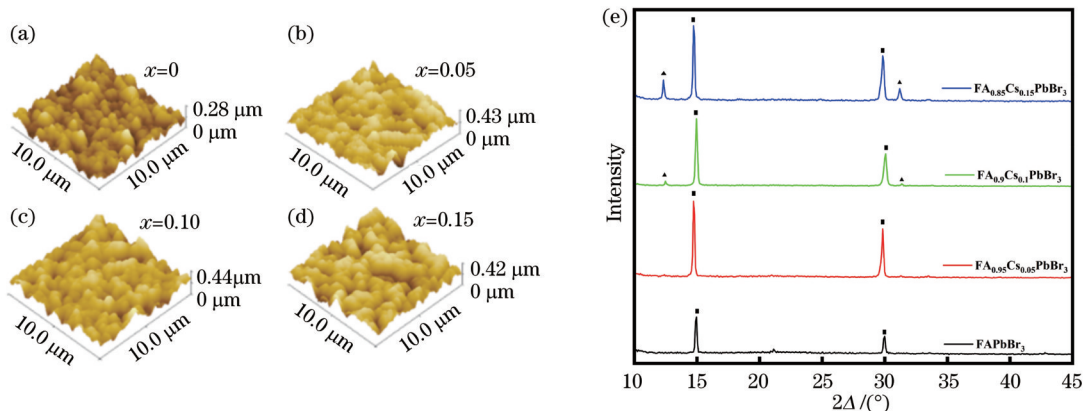


图 1 不同 Cs 掺杂浓度的 FACsPbBr_3 薄膜的基础表征。(a)~(d) 3D-AFM 图; (e) XRD 图谱

Fig. 1 Basic characterization of FACsPbBr_3 thin films with different Cs doping concentrations. (a)~(d) 3D-AFM images; (e) XRD patterns

利用椭圆偏振光谱仪分析了 FACsPbBr₃ 钙钛矿薄膜的复介电函数。图 2(a) 给出了 FA_{0.95}Cs_{0.05}PbBr₃ 薄膜在室温下的椭圆实验和模拟光谱。建模过程中采用空气/粗糙层/钙钛矿薄膜/石英基底四相光学模型进行椭圆偏分析, 其中石英基底及空气的复介电函数分别来源于空白基底测试分析和分析软件中的材料库, 粗糙层的复介电函数一般采用 Bruggeman 有效介质模型描述, 该模型在描述不同材料介质混杂时并不区分主次, 本文采用的 Bruggeman 模型中, 钙钛矿材料和空气的占比各为 50%。钙钛矿薄膜的复介电函数采用 Tauc-Lorentz 色散模型描述。Tauc-Lorentz 振子模型由 ϵ_{∞} 、 A 、 C 、 E_m 、 E_g 5 个参数确定, 这 5 个参数分别代表复介电函数的高频介电常数、振幅、展宽、峰值跃迁能量和光学带隙能量。通过改变 Tauc-Lorentz 色散模型参数、薄膜

厚度、粗糙层厚度等参数对 FACsPbBr₃ 钙钛矿薄膜的椭圆光谱进行拟合分析, 分析结果如图 2(b) 所示。复介电函数是光学材料的重要基本物理参数, 在光学材料的应用和光学器件的制造过程中发挥着重要作用。介电函数的实部与材料内部的电子极化和局域场息息相关, 而其虚部依赖于光在介质中传播时的吸收, 在高吸收区域与材料内部的电子状态和电子跃迁行为密切相关^[18-19], 因此详细研究材料的介电函数十分必要。钙钛矿薄膜复介电函数的实部和虚部幅值在低能区域变化不明显, 但在高能区域二者均随着 Cs 掺杂浓度的增加而下降。众所周知, 钙钛矿的带隙主要由 X 位掺杂决定, 而 A 位掺杂对钙钛矿带隙的影响几乎可以忽略不计^[20-21]。从图 2(b) 中可以看到, 不同 Cs 掺杂浓度的钙钛矿薄膜的带隙均位于 2.32 eV 左右。

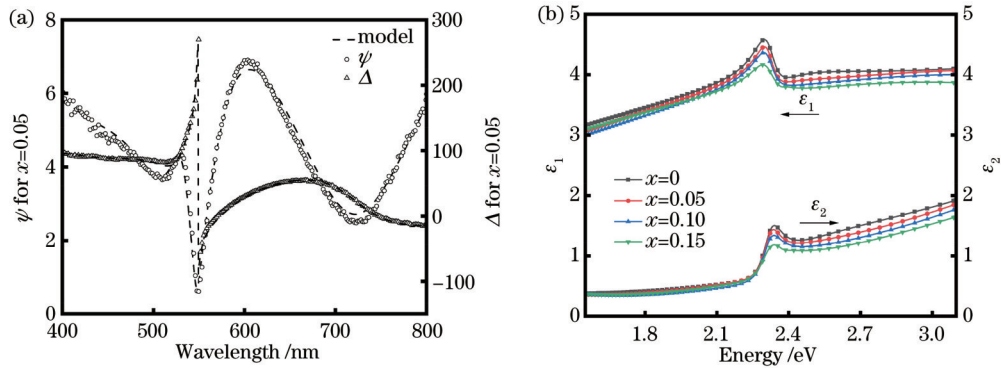


图 2 不同 Cs 掺杂浓度的 FACsPbBr₃ 薄膜的椭圆偏分析。(a) FA_{0.95}Cs_{0.05}PbBr₃ 薄膜的椭圆实验(散点)光谱和模拟(虚线)光谱; (b) 不同 Cs 掺杂浓度的 FACsPbBr₃ 薄膜的复介电函数

Fig. 2 Ellipsometry analysis of FACsPbBr₃ thin films with different Cs doping concentrations. (a) Ellipsometric experimental (dots) and simulated (dotted lines) spectra of FA_{0.95}Cs_{0.05}PbBr₃ thin film; (b) complex dielectric functions of FACsPbBr₃ thin films with different Cs doping concentrations

基于上述获取的钙钛矿薄膜复介电函数, 对结构为 Glass/FTO/TiO₂/FACsPbBr₃/spiroOMeTAD/Ag 的钙钛矿太阳能电池进行模拟优化分析, 其中超出 400~800 nm 范围的复介电函数由椭圆分析得到的最佳色散模型计算给出, 因此所得的 EQE 的模拟结果可能与实际有所误差。FACsPbBr₃ 为光吸收层和载流子产生层, 位于 FACsPbBr₃ 两侧的 TiO₂ 层和 spiro-OMeTAD 层分别为电子传输层和空穴传输层, 用于促进相应载流子的传输和阻碍相反载流子的移动, FTO 为窗口层和导电前电极。FTO、TiO₂、FACsPbBr₃ 和 spiro-OMeTAD 的厚度参考已发表文献分别选取 100 nm、43 nm、500 nm 和 200 nm^[22]。图 3 给出了不同掺杂浓度 FACsPbBr₃ 钙钛矿电池的电流密度-电压 (J - V) 特性曲线, 具体的光伏性能参数如表 1 所示。未掺杂 PSCs 的短电流密度 (J_{sc}) 为 20.59 mA/cm², 开路电势 (V_{oc}) 为 1.26 V, 填充因子 (F_F) 为 85.1%, 光电功率转换效率 (PCE) 为 22.01%。实际 PSCs 器件制备过程必然带来吸收层薄膜质量下降、深能级缺陷增加、载流子提取效率降低等问题, 使

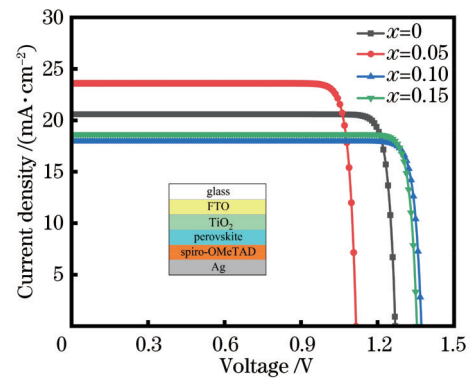


图 3 不同 Cs 掺杂浓度的 FACsPbBr₃ 太阳能电池电流密度曲线(插图为 PSCs 结构图)

Fig. 3 Current density curves of FACsPbBr₃ solar cell with different Cs doping concentrations (inset is structure diagram for PSCs)

得 F_F 降低, 因此模拟出的 PCE 相较于真实太阳能电池器件的 PCE 偏高^[23]。掺杂 Cs⁺ 后, 各掺杂 PSCs 的 F_F 值均有所提升, 当 $x=0.05$ 时, 器件的 PCE 达到最大值 23.47%, 而随着 Cs 掺杂浓度的进一步增加, PCE

表 1 不同 FACsPbBr₃ 太阳能电池的光伏参数Table 1 Photovoltaic parameters of different FACsPbBr₃ solar cell

Device parameter	$J_{sc} / (\text{mA}/\text{cm}^2)$	V_{oc} / V	$F_F / \%$	PCE / %
$x=0$	20.59	1.26	85.1	22.01
$x=0.05$	23.60	1.11	88.9	23.47
$x=0.10$	18.01	1.34	88.1	22.88
$x=0.15$	18.23	1.35	87.6	22.35

反而降低。依据 XRD 结果可知,当 x 为 0.10 和 0.15 时,钙钛矿薄膜中出现非钙钛矿 δ 相,这种缺陷或次级相的产生会降低器件的性能。

对器件性能最优的 FA_{0.95}CS_{0.05}PbBr₃ 钙钛矿薄膜进行变温椭圆偏分析,其变温复介电函数如图 4 所示。随着温度的升高,低能区域复介电函数的实部幅值减小,复介电函数虚部位于 2.32 eV 附近的跃迁峰出现明显蓝移。该跃迁峰为钙钛矿的光学带隙,源于 Pb 6s 和 Br 4p 轨道构成的反键态(价带顶)和 Pb 6p 和 Br 4s 轨道构成的非键态(导带底)之间的直接光学跃迁^[24-25]。为更准确地分析光学带隙随温度的变化,运用临界点模型拟合了复介电函数虚部的二阶导数谱,并利用吸收光谱计算了光学带隙,结果如图 5(a) 所示。如图 5(a) 和 (b) 所示,室温(303 K)下利用椭圆偏

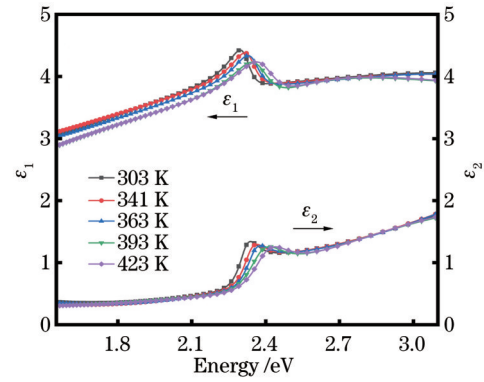


图 4 不同温度下的 FA_{0.95}CS_{0.05}PbBr₃ 薄膜的复介电函数
Fig. 4 Complex dielectric functions of FA_{0.95}CS_{0.05}PbBr₃ thin film with different temperature

振光谱获取的光学带隙为 2.32 eV,利用吸收光谱计算得到的光学带隙为 2.33 eV,二者相符,这进一步证明了椭圆偏分析的准确性。此外,随着温度的升高,光学带隙几乎呈现线性变化,如图 5(b) 所示。温度升高导致晶格膨胀以及电子声子耦合效应增强,使得导带和价带的能量均随着温度的升高而降低,而前者降低得更明显,因此带隙表现出蓝移现象。在 393 K 时,从图 5(b) 可以观察到明显的相变,钙钛矿由正交相(O)转变为四方相(T),这与之前的报道相一致^[26]。

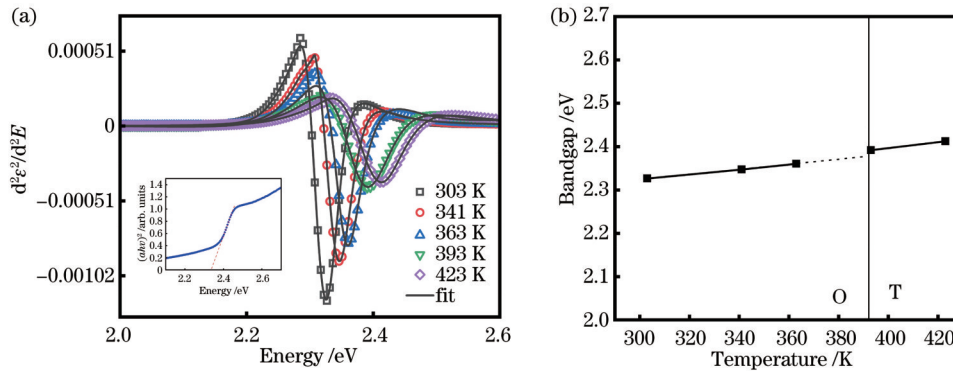


图 5 不同温度下 FA_{0.95}CS_{0.05}PbBr₃ 薄膜的光学性质。(a) 复介电函数虚部的二阶导数谱及其拟合曲线,插图为利用常温下吸收谱计算得到的光学带隙;(b) 四方相和正交相时带隙的温度依赖关系

Fig. 5 Optical properties of FA_{0.95}CS_{0.05}PbBr₃ at different temperature. (a) Second-derivative of imaginary parts of complex dielectric function, and inset is bandgap calculated by absorption spectrum; (b) temperature-dependence bandgaps of FA_{0.95}CS_{0.05}PbBr₃ for tetragonal and orthorhombic phases

对结构为 Glass/FTO (100 nm)/TiO₂ (43 nm)/FA_{0.95}CS_{0.05}PbBr₃ (500 nm)/spiroOMeTAD (200 nm)/Ag 的 PSCs 进行 EQE 模拟并对其中的光学损失进行分析,结果如图 6(a) 所示。FA_{0.95}CS_{0.05}PbBr₃ 太阳能电池中器件的反射为器件电流损失的最大来源,占比达到 11.2%,而 FTO 的寄生吸收也是造成器件电流损失的主要原因之一,这与已报道的结果相符^[27]。此外 TiO₂ 电子传输层和金属 Ag 电极也存在一定的光吸收损失,若想获得高效率的太阳能电池,需要尽量降低各部分的吸收损失。考虑器件运行时的环境温度对器件

性能的影响,模拟了不同温度下的 FA_{0.95}CS_{0.05}PbBr₃ 太阳能电池的 EQE 谱,结果如图 6(b) 所示。从图 6(b) 中可以看出,温度升高使 PSCs 器件在近红外区光吸收能力以及载流子传输能力降低,光学带隙随温度的升高而增加,从而使器件的整体响应带宽减小,影响了器件的光学性能。更进一步,研究了温度和 FA_{0.95}CS_{0.05}PbBr₃ 吸收层厚度对太阳能电池 J_{sc} 的影响。从图 6(c) 中可以看出, J_{sc} 随吸收层厚度的增加而单调增加,当吸收层厚度小于 400 nm 时, J_{sc} 随厚度的增加有较大的提升,而在 400~800 nm 的厚度范围内,随着

厚度的增加, J_{sc} 变化率减小, 当厚度大于 800 nm 时, 增加吸收层厚度已不能明显提升电池的短路电流密度。考虑到吸收层的厚度也会影响开路电压, 过厚的吸收层会导致开路电压的降低, 因此需综合器件的各个光伏参数, 选取适当的钙钛矿吸收层厚度。本研究在考虑钙钛矿吸收层厚度的同时, 也考虑了温度的因素。

以厚度为 800 nm 钙钛矿吸收层为例, 可以看到温度升高会使太阳能电池的短路电流增大, 但是增幅有限, 且当吸收层过厚或者过薄时, 温度对短路电流的影响进一步降低。器件工作温度变化时, 钙钛矿太阳能电池的短路电流降低得较小。

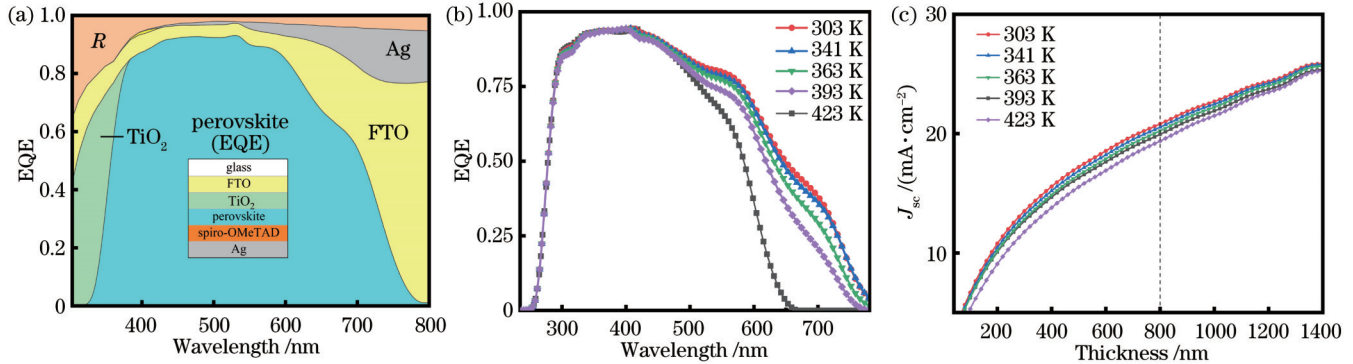


图 6 $FA_{0.95}Cs_{0.05}PbBr_3$ 薄膜的器件模拟。(a) $FA_{0.95}Cs_{0.05}PbBr_3$ 的 EQE 曲线, 以及 Glass/FTO (100 nm)/ TiO_2 (43 nm)/ $FA_{0.95}Cs_{0.05}PbBr_3$ (500 nm)/spiro-OMeTAD (200 nm)/Ag 结构太阳能电池中各层的 $1-R$ 曲线; (b) 不同温度下 $FA_{0.95}Cs_{0.05}PbBr_3$ 吸收层的 EQE 曲线; (c) $FA_{0.95}Cs_{0.05}PbBr_3$ 太阳能电池的 J_{sc} 值随温度和吸收层厚度的变化关系

Fig. 6 Simulation of $FA_{0.95}Cs_{0.05}PbBr_3$ films. (a) EQE spectrum of $FA_{0.95}Cs_{0.05}PbBr_3$ layer and $1-R$ of component layers in Glass/FTO (100 nm)/ TiO_2 (43 nm)/ $FA_{0.95}Cs_{0.05}PbBr_3$ (500 nm)/spiro-OMeTAD (200 nm)/Ag structure; (b) EQE spectrum of $FA_{0.95}Cs_{0.05}PbBr_3$ layer at different temperatures; (c) J_{sc} values for PSCs with thickness of $FA_{0.95}Cs_{0.05}PbBr_3$ from 0 to 1400 nm at different temperatures

4 结 论

通过一步反溶剂法制备了高质量的 Cs 掺杂 $FA_{1-x}Cs_xPbBr_3$ ($x=0, 0.05, 0.10, 0.15$) 钙钛矿薄膜。分别通过椭圆偏振光谱和吸收光谱研究了 $FACsPbBr_3$ 薄膜的复介电函数、吸收系数, 以及变温复介电函数等光学性质。利用椭圆偏振光谱和吸收光谱获取的室温下 $FA_{0.95}Cs_{0.05}PbBr_3$ 薄膜的光学带隙相一致。基于椭圆偏振测量得到的复介电函数, 进一步模拟分析了 $FACsPbBr_3$ 太阳能电池的性能。结果表明, Cs 掺杂可以提高器件的性能, 当 $x=0.05$ 时, 器件的 PCE 最高可达 23.47%, 而 Cs 掺杂浓度过高又会引入非钙钛矿 δ 相, 导致器件性能降低。通过 $FA_{0.95}Cs_{0.05}PbBr_3$ 太阳能电池的变温椭圆偏振光谱分析和变温 EQE 光谱 (303~423 K) 模拟可以发现, 带隙随着温度的升高而增大, 且在 393 K 时, 钙钛矿由正交相变为四方相。器件的最高效率随着温度的升高而微弱降低, 器件的短路电流随着温度的升高而增大, 但增幅有限。器件在近红外区的光吸收能力随着温度的升高而降低, 带隙的增加导致了整体响应带宽的减小。综合考虑器件光学性能和稳定性, 发现 $x=0.05$ 的 $FACsPbBr_3$ 钙钛矿太阳能电池具有较好的光伏性能。

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Temperature-Dependent Optical Properties and Photovoltaic Device Design of Cs-Doped FAPbBr₃ Thin Films

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Abstract

Objective Perovskite solar cells (PSCs) have attracted considerable research interest due to their large absorption coefficients, long diffusion lengths, tunable bandgap, and high charge mobility. The power conversion efficiency (PCE) of PSCs has increased from 3.8% in 2009 to 26.08% in 2023. However, their mass-scale production is limited by the inherent instability of the perovskites, which decompose easily during reaction with moisture, oxygen, light and heat. Formamidinium-cesium (FAC) mixed cations perovskites have demonstrated excellent thermal stability and suitable bandgap for solar spectrum absorption. On the other hand, the carrier mobility of Br⁻ is higher than that of I⁻. Therefore, we choose Cs-doped FA_{1-x}Cs_xPbBr₃ (FACsPbBr₃) thin films to study optical properties and construct high-efficient and stable PSCs. However, experimental PCE verification of PSCs is costly and time-consuming. Numerical simulation provides a simple and effective way to evaluate the PSCs performance and explore new possible device architectures. The complex dielectric function is an important optical parameter. Fundamentally, the complex dielectric functions are critical for simulating the external quantum efficiency (EQE) of the PSCs. Furthermore, determining the bandgap from the complex dielectric functions provides information on the band structure and enables the detection of temperature-dependent phase changes. We prepare Cs-doped FA_{1-x}Cs_xPbBr₃ (x=0, 0.05, 0.10, 0.15) perovskite thin films and study the corresponding complex dielectric functions by spectroscopic ellipsometry (SE). The resultant complex dielectric functions are then employed to simulate EQE. Meanwhile, the temperature-dependent EQE simulation of FA_{0.95}Cs_{0.05}PbBr₃ PSC is

also performed. We hope that the basic findings can help design highly efficient and stable PSCs and understand the relationship between the complex dielectric functions and EQE of PSCs.

Methods FACsPbBr₃ thin films with different Cs doping concentrations are prepared by one-step anti-solvent method, and the surface morphology of samples is characterized by atomic force microscopy (AFM). Additionally, the crystal structure of the samples is studied using a D8 Advance X-ray diffractometer, and the effects of Cs-doped concentrations on the surface morphology and crystal structure of the prepared samples are investigated. The optical properties of the samples are analyzed by SE. The resultant complex dielectric functions are adopted to simulate the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE of the devices. The doping effects on the PSCs performance are discussed in detail. Next, the temperature-dependent ellipsometric measurements (303–423 K) and room temperature absorption measurement of the sample with the highest simulated EQE are performed. Based on the temperature-dependent complex dielectric functions, the influence of temperature and absorber thickness on both the simulated EQE and the short-circuit current density of the device is studied.

Results and Discussions The prepared FACsPbBr₃ thin films exhibit smooth and compact surface morphology with pebble stone-like structures, indicating the high quality of the samples (Fig. 1). When the doping concentration increases to 0.1, the appearance of the δ -phase non-perovskite structure is observed in the XRD pattern (Fig. 1). The ellipsometric measurements show that the amplitude of the complex dielectric functions decreases with the increasing doping concentrations (Fig. 2). The EQE simulation shows that Cs doping improves the PCE, but excessive Cs doping degrades PCE of the devices, which might be attributed to the appearance of the δ -phase. The maximum PCE can reach up to 23.47% under the doping concentration of $x=0.05$ (Table 1). Furthermore, an increase in bandgap with the rising temperature is observed based on the temperature-dependent dielectric functions of FA_{0.95}Cs_{0.05}PbBr₃. Additionally, an orthogonal-tetragonal phase transition is observed around 393 K (Fig. 5). The temperature-dependent EQE simulation of FA_{0.95}Cs_{0.05}PbBr₃ perovskite solar cell shows that the maximum PCE of the device can stabilize at about 23.47% and exhibits little dependence with temperature. However, there is a rapid EQE decrease in the near-infrared region with the increasing temperature, which reduces the device bandwidth (Fig. 6).

Conclusions We prepare Cs-doped FA_{1-x}Cs_xPbBr₃ ($x=0, 0.05, 0.10, 0.15$) perovskite thin films by a one-step anti-solvent method. The complex dielectric functions of FACsPbBr₃ thin films are studied by SE, and the temperature-dependent complex dielectric functions and absorption spectra of FA_{0.95}Cs_{0.05}PbBr₃ are researched by spectroscopic ellipsometry and UV-visible spectrophotometer respectively. The optical bandgaps obtained by SE are consistent with that obtained by absorption spectra. The EQE simulation results show that Cs doping can improve the device performance. When the doping concentration is 0.05, the PCE can reach up to 23.47%, but excessive Cs doping concentration will introduce non-perovskite δ -phase, decreasing the device performance. According to temperature-dependent ellipsometric measurements, we find that the bandgap increases with the rising temperature, and there is an obviously orthorhombic-tetragonal phase transition at about 393 K. With the increasing temperature, the device PCE slightly decreases, while the short-circuit current slightly increases. However, the light absorption capability of the device in the NIR region obviously reduces with the increasing temperature. The response bandwidth reduction could be attributed to the increased bandgap. Thus, by considering the performance and stability of the devices, FACsPbBr₃ PSCs with a Cs-doped concentration of 0.05 have the best overall photovoltaic performance.

Key words thin films; Cs-doped perovskite; optical properties; temperature-dependent ellipsometry spectrum; external quantum efficiency simulation