金属离子替换的有机-无机钙钛矿太阳能电池及其迟滞现象

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摘要 注入金属离子替换有机-无机钙钛矿中参与成键的 Pb^{2+} 可以有效调控其结晶动力学、薄膜形貌和光电特性, 因此, 通过优化 Pb^{2+} 替换比例提高钙钛矿太阳能电池性能是当前的研究热点之一. 但是, Pb^{2+} 替换对器件异常迟滞现象的影响却缺乏深入的研究. 本文采用 Cd^{2+} 替换的 MAPbI_3 为模型体系, 研究了不同 Cd^{2+} 浓度下 MAPbI_3 材料性质及其平面异质结光伏器件(结构为 $\text{ITO}/\text{NiO}_x/\text{Cd-MAPbI}_3/\text{PCBM}/\text{Ag}$)性能的变化趋势. 研究表明, 优化比例(0.5%)的 Cd^{2+} 可以有效增强材料结晶性、改善薄膜形貌, 降低非辐射复合, 提高光生载流子寿命, 从而大幅提高器件性能. 而 Cd^{2+} 替换比例过高(>2.5%)时, 钙钛矿薄膜中不仅会出现相分离阻碍电荷传输, 而且其非辐射复合加剧, 光生载流子寿命降低, 最终导致器件性能下降. 与此同时, 过量的 Cd^{2+} 注入还会引起严重的迟滞现象, 利用扫描开尔文探针显微镜(SKPM)证实这一现象与钙钛矿薄膜中显著的离子迁移有关.

关键词 有机-无机钙钛矿太阳能电池, 金属离子替换, 平面异质结, 异常迟滞现象, 离子迁移, 扫描开尔文探针显微镜

近年来, 有机-无机钙钛矿材料由于其载流子扩散距离长^[1,2]、缺陷容忍度高^[3]、吸收光谱可调^[4]等优点, 使其在太阳能电池中的应用前景被广泛看好, 短短十年时间, 电池的能量转换效率(PCE)从最初的3.8%提升到超过23%^[5~22]. 有机-无机钙钛矿的化学通式为 ABX_3 , 其中A代表正一价有机阳离子(如 CH_3NH_3^+ (MA^+), $\text{HC}(\text{NH}_2)_2^+$ (FA^+)等), B代表正二价金属阳离子(如 Pb^{2+} , Sn^{2+} 等), X代表负一价卤素阴离子(如 Cl^- , Br^- , I^-). 理论计算表明, Pb^{2+} 参与成键, 是决定钙钛矿结晶动力学、薄膜形貌和光电特性的重要因素之一^[23,24]. 因此,

大量文献报道通过 Pb^{2+} 替换, 包括等价替换(Sn^{2+} , Sr^{2+} , Cd^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ba^{2+} , Zn^{2+} , Se^{2+} 和 Eu^{2+} 等)^[25~34]和非等价替换(Cu^+ , Na^+ , Ag^+ , In^{3+} , Sb^{3+} , Al^{3+} 和 Bi^{3+} 等)^[35~39], 可以调控钙钛矿的结晶性、薄膜形貌、能带结构和光生载流子动力学等, 从而达到优化器件性能的目的. 但是, Pb^{2+} 替换对于钙钛矿太阳能电池特有的异常迟滞现象的影响却缺乏深入的研究.

我们的前期工作使用 Ag^+ 替换 Pb^{2+} 后发现, 较小的 Ag^+ 浓度(<1.0%)可以显著提升器件性能, 而进一步增加 Ag^+ 浓度不仅会导致器件性能大幅衰减而且会引起

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严重的迟滞现象^[36]。我们认为过量的 Ag^+ 替换 Pb^{2+} 后, 为了保持钙钛矿电中性易形成 Γ 空位缺陷, 一方面会增加载流子复合几率使得器件性能下降, 另一方面可能导致离子迁移加剧迟滞效应。为避免非等价替换可能带来的 Γ 空位缺陷的干扰, 本文以 Cd^{2+} 替换的 MAPbI_3 钙钛矿为模型体系, 深入研究 Pb^{2+} 替换比例与器件性能及迟滞现象之间的联系。与注入 Ag^+ 后的器件行为类似, 优化的 Cd^{2+} 替换比例能够提高器件性能, 而注入过量的 Cd^{2+} 会导致器件性能变差且伴随严重的迟滞现象。我们使用扫描开尔文探针显微镜证实, 注入过量的 Cd^{2+} 加剧钙钛矿薄膜中的离子迁移, 可能是引起器件异常迟滞现象的重要因素之一。

1 实验

1.1 原料

碘甲烷(MAI)购买于西安宝莱特公司, 碘化铅(PbI_2 , 99.9%)和二甲亚砜(DMSO, 99.9%)购买于阿法埃莎化学有限公司, 甲苯、氯苯、乙醇胺和碘化镉(CdI_2 , 99.9%)购买于西格玛奥德里奇贸易有限公司, [6,6]-苯基- C_{60} -丁酸异甲酯(PCBM)购买于美国ADS公司, γ -丁内酯(GBL)购买于阿拉丁试剂有限公司, 四水合乙酸镍($\text{Ni}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, 99.9%)购买于北京伊诺凯科技有限公司, 乙醇、丙酮和异丙醇购买于国药集团化学试剂有限公司。氧化铟锡(ITO)玻璃衬底购买于厦门惟华光能有限公司, Ag 颗粒购买于中诺新材北京有限公司。

1.2 器件制备

(i) 前驱体溶液的配制。 Cd^{2+} 替换的钙钛矿前驱体溶液 $\text{MACd}_x\text{Pb}_{1-x}\text{I}_3$ (1 mol/L)是按 $x:1:1-x$ ($0 \leq x \leq 0.05$)的摩尔比例称取 CdI_2 , MAI和 PbI_2 固体粉末后加入体积比为7:3的GBL和DMSO混合溶剂配制的, 接着转移至手套箱内并在60℃的热台上搅拌2 h后过滤备用。

MACdI_3 和 MA_2CdI_4 前驱体溶液(1 mol/L)分别是按1:1和1:2的摩尔比例称取 CdI_2 和MAI固体粉末后加入体积比为7:3的GBL和DMSO混合溶剂配制的, 接着转移至手套箱内并在60℃的热台上搅拌2 h后过滤备用。

NiO_x 前驱体溶液是称取124.42 mg $\text{Ni}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ 后加入5 mL乙醇和30 μL 乙醇胺配制的, 接着在空气中70℃的热台上搅拌4 h后过滤备用。

(ii) 钙钛矿太阳能电池器件的制备。将ITO玻璃基底依次在玻璃水、去离子水、乙醇、丙酮和异丙醇中

超声15 min, 然后用氮气枪小心吹干, 再用氧等离子处理10 min。接着将 NiO_x 溶液滴在ITO玻璃基底上, 以4000 r/min的转速旋涂60 s, 旋涂结束后在大气氛围下的400℃热台上退火1 h。随后将样品转移至氮气手套箱内, 取50 μL 钙钛矿前驱体溶液滴在ITO/ NiO_x 上, 以500 r/min, 5 s, 1000 r/min, 10 s和4000 r/min, 40 s的方式连续旋涂55 s, 并在旋涂过程的第40 s时滴加500 μL 的甲苯对钙钛矿薄膜进行处理, 之后在100℃的热台上退火10 min。取40 μL 的PCBM溶液(20 mg/mL)滴在钙钛矿层上, 以1500 r/min旋涂60 s。最后将样品转移至真空蒸镀设备中, 在 4×10^{-4} Pa下蒸发100 nm的 Ag 电极完成器件制备, 器件面积为0.12 cm^2 。

1.3 表征

器件的电流密度-电压(J - V)曲线是在光强度为100 mW/cm^2 的AM 1.5G的模拟太阳光下通过Keithley 2400源表进行测定, 该测试是在手套箱中完成。外量子效率(EQE)是采用由Merlin 70104(Newport, 美国)的数字锁相辐射测量系统、300 W氙灯以及74125 Oriel Cornerstone 260 1/4 m单色仪构成的太阳能电池光谱响应系统进行测量的。钙钛矿薄膜的X射线衍射(XRD)图谱是采用以 $\text{Cu K}\alpha$ 射线作为入射光源的D8(Bruker, 美国)进行测量的。钙钛矿薄膜的扫描电子显微镜(SEM)图像是使用Quanta 400 FEG(FEI, 美国)进行表征。紫外-可见光吸收谱(UV-Vis)是用Lambda 750(PerkinElmer, 美国)测量的。稳态荧光光谱(PL)是利用配有56RCS001/HV(Melles Griot, 美国)光源、SP2500i/SP2300i(Princeton Instruments, 美国)分光计和PIXIS256(Princeton Instruments, 美国)探测器的自制系统进行测定的, 其中激发波长为532 nm。采用FLS920(Edinburgh Instruments, 英国)对钙钛矿薄膜的瞬态PL进行表征, 其中激发波长为507 nm, 检测波长为770 nm。扫描开尔文探针显微镜(SKPM)使用的是氮气手套箱中的Cypher S(Asylum Research, Oxford Instruments, 美国)原子力显微镜, 与传统两步扫描模式的差异是第一遍扫描形貌的同时在针尖上外加直流偏压 V_{bias} 用于诱导样品内部的离子迁移, 第二遍扫描是在第一遍形貌曲线的基础上抬高10 nm后测量样品的表面电势^[40]。

2 结果与讨论

我们利用XRD和SEM对钙钛矿的结晶质量和薄膜形貌进行了表征。图1展示了 Cd^{2+} 替换 Pb^{2+} 前后 MAPbI_3

薄膜以及可能的衍生物的XRD图谱. 从图1(a)中可以看出, MAPbI₃在 $2\theta=14.12^\circ$ 和 28.44° 处有两个较强的衍射峰, 在 $2\theta=19.94^\circ$, 23.46° , 24.48° 处有3个较弱的衍射峰, 这些衍射峰分别对应于MAPbI₃的(110), (220), (112), (211)和(202)晶面. 当Cd²⁺替换浓度从0%增加到1.0%时, (110)和(220)面的衍射峰强度逐渐增大, 半高宽逐渐变窄, 这表明Cd²⁺注入后薄膜结晶性提高, 晶粒变大. 当Cd²⁺替换浓度超过2.5%后, 在 $2\theta=12.70^\circ$ 处出现了PbI₂(001)面的衍射峰, 与此同时还伴随钙钛矿衍射峰强逐渐减弱. 我们还发现当Cd²⁺替换浓度为5.0%时, 在 $2\theta=16.68^\circ$ 处出现了新的衍射峰. 为了澄清产生此衍射峰的原因, 我们首先配备了MACdI₃和MA₂CdI₄的前驱体溶液, 随后分别在旋涂过程中滴加甲苯和不滴加甲苯制备薄膜. 从图1(b)的XRD图谱可以证实, 不滴加甲苯时, 仅MA₂CdI₄薄膜在 $2\theta=16.68^\circ$ 处有衍射峰, 该衍射峰源于MA₂CdI₄(002)面的衍射. 但滴加甲苯时MACdI₃在 $2\theta=16.68^\circ$ 处也出现了衍射峰, 表明部分MACdI₃转变为MA₂CdI₄, 而这正是制备Cd²⁺替换MAPbI₃薄膜所采用的工艺. 因此, 加入5.0%浓度的Cd²⁺替换Pb²⁺时, 钙钛矿薄膜易析出PbI₂和MA₂CdI₄, 结合钙钛矿衍射峰强度减弱可以表明钙钛矿结晶质量下降. 图2展示了Cd²⁺替换Pb²⁺前后MAPbI₃薄膜的SEM形貌图. 当Cd²⁺替换浓度从0%增加到0.5%时, 薄膜表面保持均匀, 没有出现孔洞, 同时晶粒尺寸逐渐增大, 这与图1(a)中(110)面衍射峰半高宽的变窄相对应, 说明Cd²⁺替换Pb²⁺有利于改善钙钛矿薄膜的形貌. 当Cd²⁺替换浓度超过1.0%后, 晶粒继续增大, 但薄膜中开始出现孔洞和亮白区域, 结合图1(b)可知这些物质可能为析出的PbI₂和MA₂CdI₄. 通常认为产生这种亮白区域是由于该区域的物质导电性较差而引起了电荷积累^[41], 不利于电荷传输.

我们进一步研究了材料的光吸收和光致发光特性. 图3(a)展示了Cd²⁺替换Pb²⁺前后MAPbI₃薄膜的UV-Vis吸收光谱. 可以看出, 在400~800 nm的长波段范围内, 不同Cd²⁺替换浓度的钙钛矿薄膜光吸收强度基本保持不变, 仅当Cd²⁺浓度为5.0%时, 在400 nm以下的短波段, 薄膜的光吸收有明显的下降, 可能是源于晶体质量变差. 我们对图3(a)中的UV-Vis吸收光谱做Tauc plot处理, 结果如图3(b)所示, 可以看出, 当Cd²⁺浓度小于1.0%时, 光学带隙基本不变, 当Cd²⁺浓度大于2.5%时光学带隙变窄. 为了进一步理解Cd²⁺替换Pb²⁺对薄膜光致发光特性的影响, 我们对钙钛矿薄膜进行了稳态和瞬态的荧光光谱测试. 图3(c)展示了Cd²⁺替换Pb²⁺前后MAPbI₃薄

图1 (网络版彩色)Cd²⁺替换MAPbI₃薄膜及可能的衍生物的XRD图谱. (a) 不同Cd²⁺替换浓度(0%, 0.2%, 0.5%, 1.0%, 2.5%和5.0%)下MAPbI₃薄膜的XRD图谱; (b) Cd²⁺替换浓度0%, 5.0%下MAPbI₃薄膜, CdI₂薄膜, 以及反溶剂清洗与否的MACdI₃和MA₂CdI₄薄膜的XRD图谱

Figure 1 (Color online) XRD spectra of Cd-incorporated MAPbI₃ films and other possible derivatives. (a) XRD spectra of MAPbI₃ films with different Cd²⁺ concentrations (0%, 0.2%, 0.5%, 1.0%, 2.5% and 5.0%); (b) XRD spectra of MAPbI₃ films with Cd²⁺ concentration of 0%, 5.0%, CdI₂ films, and MACdI₃, MA₂CdI₄ films with or without solvent washing

膜的稳态PL光谱. 当Cd²⁺替换浓度从0%增加到0.5%时, 钙钛矿薄膜的荧光发射峰强度逐渐增加, 说明Cd²⁺替换可以有效地降低光照时薄膜中载流子的非辐射复合. 但是当Cd²⁺替换浓度继续从1.0%增加到5.0%时, 荧光发射峰强度反而逐渐减小, 意味着薄膜中的非辐射复合逐渐增强, 当替换浓度大于2.5%以后荧光发射峰发生红移, 这与图3(b)中其光学带隙变窄相吻合. 图3(d)展示了不同Cd²⁺替换浓度下MAPbI₃薄膜的瞬态PL光谱, 并通过双指数函数拟合得到荧光寿命^[42](表1). 可以发现, 当Cd²⁺替换浓度从0%增加到0.5%时, 光生载流子平均寿命不断增加, 由19.81 ns逐渐增加到69.63 ns. 继续增加Cd²⁺替换浓度到5.0%, 光生载流子平均寿命不

图2 不同 Cd^{2+} 替换浓度下 MAPbI_3 薄膜的SEM图. (a) 0%; (b) 0.2%; (c) 0.5%; (d) 1.0%; (e) 2.5%; (f) 5.0%, 图中标尺为500 nm

Figure 2 SEM images of MAPbI_3 films with Cd^{2+} concentrations of 0% (a), 0.2% (b), 0.5% (c), 1.0% (d), 2.5% (e) and 5.0% (f). Scale bars are 500 nm

断减小, 由69.63 ns逐渐减小到24.89 ns.

以不同 Cd^{2+} 替换浓度的 MAPbI_3 薄膜为活性层, 我

们制备了反式结构平面异质结钙钛矿太阳能电池, 电池结构如图4(a)所示. 图4(b)和表2分别是不同 Cd^{2+} 替换浓度下钙钛矿太阳能电池的 $J-V$ 曲线图和光伏性能参数表. 从光伏测试结果中可以看出, Cd^{2+} 替换浓度从0%提高至0.5%时, 电池的短路电流和填充因子逐渐提升, 能量转化效率也随之提高. 当替换浓度为0.5%时, 电池的PCE由15.38%(其中, 开路电压(V_{OC})为1.08 V, 短路电流(J_{SC})为19.24 mA/cm^2 , 填充因子(FF)为0.74)提升至17.01%(其中, V_{OC} 为1.09 V, J_{SC} 为20.01 mA/cm^2 , FF为0.78), 这得益于 Cd^{2+} 替换后薄膜结晶质量的提高、晶粒尺寸的增大、非辐射复合的降低和载流子平均寿命的增加. 继续提高 Cd^{2+} 替换浓度, 电池的开路电压、短路电流、填充因子和转化效率都逐渐减小, 主要是因为钙钛矿的晶体质量下降、薄膜形貌变差、出现相分离阻碍载流子传输、非辐射复合增加以及光生载流子平均寿命减小. 图4(c)是不同 Cd^{2+} 替换浓度下钙钛矿太阳能电池的EQE曲线. 我们发现, 当 Cd^{2+} 替换浓度在0.2%~1.0%时, 电池在580~750 nm范围内的外量子效率有所提升, 而其他波段基本上与0%时重合, 因此 Cd^{2+} 替换后电池短路电流的增加主要来源于此波段外量子效率的提升. 之前通过图3(a)得知不同 Cd^{2+} 替换浓度的钙钛矿薄膜在光学吸收上并无明显差异, 所以EQE在580~750 nm波段的增加应主要来自于薄膜结晶

图3 (网络版彩色)不同 Cd^{2+} 替换浓度下 MAPbI_3 薄膜的UV-Vis吸收光谱(a)、Tauc plot图(b)、稳态PL光谱(c)和时间分辨PL光谱(d)

Figure 3 (Color online) Absorption spectra (a), Tauc plot (b), normalized steady-state PL spectra (c) and time-resolved PL spectra (d) of MAPbI_3 films with different Cd^{2+} concentrations on glass substrate

表1 不同 Cd^{2+} 替换浓度的 MAPbI_3 薄膜荧光寿命Table 1 PL lifetime of Cd-incorporated MAPbI_3 films

Cd(%)	$A_1/(A_1+A_2)(\%)^{a)}$	$\tau_1(\text{ns})^{a)}$	$A_2/(A_1+A_2)(\%)^{a)}$	$\tau_2(\text{ns})^{a)}$	$\tau_{\text{avg}}(\text{ns})^{b)}$
0	24.95	72.13	75.05	2.41	19.81
0.2	41.22	112.54	58.78	3.29	48.32
0.5	51.79	130.12	48.21	4.64	69.63
1.0	35.20	113.15	64.80	2.36	41.36
2.5	37.38	96.51	62.62	3.36	38.17
5.0	29.77	76.97	70.23	2.81	24.89

a) 拟合公式: $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$; b) 载流子平均寿命: $\tau_{\text{avg}}=\tau_1\times[A_1/(A_1+A_2)]+\tau_2\times[A_2/(A_1+A_2)]$

图4 (网络版彩色) Cd^{2+} 替换 MAPbI_3 太阳能电池性能和迟滞现象表征. (a) Cd^{2+} 替换钙钛矿太阳能电池的结构示意图; (b) AM 1.5G光照下以0.1 V/s速率正向扫描得到的不同 Cd^{2+} 替换浓度的 MAPbI_3 太阳能电池的 J - V 曲线; (c) 不同 Cd^{2+} 替换浓度的 MAPbI_3 太阳能电池的EQE曲线; (d)~(i)不同 Cd^{2+} 替换浓度(0%, 0.2%, 0.5%, 1.0%, 2.5%, 5.0%)的 MAPbI_3 太阳能电池在不同扫描速率(0.01, 0.1和1.0 V/s)以及正(从0~1.2 V)反(从1.2~0 V)两个扫描方向下得到的 J - V 曲线

Figure 4 (Color online) Device performance and hysteresis behavior of Cd-incorporated MAPbI_3 solar cells. (a) The device structure of Cd-incorporated MAPbI_3 solar cells; (b) J - V curves of Cd-incorporated MAPbI_3 solar cells under AM 1.5G illumination at forward scan rate of 0.1 V/s; (c) the corresponding external quantum efficiency curves; (d)~(i) J - V hysteresis measurement of Cd-incorporated MAPbI_3 devices with Cd^{2+} concentration of 0% (d), 0.2% (e), 0.5% (f), 1.0% (g), 2.5% (h), 5.0% (i) at different scan rates (0.01, 0.1, 1 V/s) and scan direction (forward scan is from 0 to 1.2 V, backward scan is from 1.2 to 0 V)

质量的提高和晶粒尺寸的增加, 而400~580 nm波段处的EQE已经接近甚至超过90%, 薄膜结晶质量的提高

和晶粒尺寸的增加对其提升效果不明显. 当 Cd^{2+} 替换浓度大于1.0%时, EQE开始逐渐降低, 这与电池性能衰

表 2 不同Cd²⁺替换浓度的MAPbI₃太阳能电池的光伏性能参数

Table 2 Photovoltaic parameters of Cd-incorporated MAPbI₃ solar cells at forward scan rate of 0.1 V/s

Cd(%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE(%)
0	1.08	19.24	0.74	15.38(14.68±0.67)
0.2	1.08	19.64	0.75	15.89(15.13±0.66)
0.5	1.09	20.01	0.78	17.01(16.36±0.59)
1.0	1.08	19.51	0.74	15.60(14.72±0.84)
2.5	1.03	15.46	0.60	9.55(8.64±0.89)
5.0	0.99	11.59	0.42	4.82(3.77±1.01)

减的原因类似。EQE的变化趋势和*J-V*测试的*J_{sc}*结果吻合。进一步地,我们研究了电压扫描速率(1.0, 0.1, 0.01 V/s)和扫描方向(从0~1.2 V为正向扫描,从1.2~0 V为反向扫描)对不同Cd²⁺替换浓度下电池性能的影响。我们参照文献[43]报道的迟滞因子(Hysteric index, HI)公式:

$$HI = \frac{|J_{scan-}(V_{oc}/2) - J_{scan+}(V_{oc}/2)|}{J_{scan-}(V_{oc}/2)}, \quad (1)$$

*J_{scan-}*是反扫时在*V_{oc}/2*处的光电流, *J_{scan+}*是正扫时在*V_{oc}/2*处的光电流,定量比较Cd²⁺替换Pb²⁺前后器件的迟滞效应。结合图4(d)~(i)和表3可以看出,当Cd²⁺替换浓度在0.2%~1.0%时, *J-V*曲线的迟滞现象较小, HI值在不同扫描速率下的变化也相对较小,但是当Cd²⁺替换浓度超过1.0%后, *J-V*曲线的迟滞现象开始显现, HI也显著增加,且随着扫描速率的增加而增大。

为了进一步理解Cd²⁺替换Pb²⁺后器件产生迟滞现象的原因,我们使用两步扫描模式SKPM^[44-56]并在第一步形貌扫描时施加直流偏压*V_{bias}*来测量不同Cd²⁺替换浓度下钙钛矿薄膜表面电势的变化趋势^[40]。测试原理如图5(a)所示。图5(c)~(e)表示在-1, 0 和1 V三种直流偏压下,不同Cd²⁺替换浓度钙钛矿薄膜的形貌图和表面电势分布图,所有偏压下的平均电势总结于图5(b)中。从形貌图上,我们看到随Cd²⁺浓度增大晶粒逐渐变大,这与XRD和SEM的结果一致。从电势图中,我们发现当Cd²⁺替换比例为0%和0.5%时,薄膜的平均表面电势基本不随*V_{bias}*变化。而当替换比例提高至5.0%时,薄膜的平均表面电势在不同*V_{bias}*诱导下出现明显变化。Yun等人^[40]也报道了钙钛矿薄膜表面电势随形貌扫描时施加的直流偏压变化而改变的现象,并认为此现象源于直流偏压诱导下离子迁移并积累在薄膜表面导致表面电势的变化。我们推测,2.5%~5.0%浓度的Cd²⁺替

表 3 不同Cd²⁺替换浓度的MAPbI₃太阳能电池在不同扫描速率(s)下的迟滞因子

Table 3 Hysteric index of different Cd-incorporated MAPbI₃ solar cells at different scan rates

Cd(%)	HI(<i>s</i> =1 V/s)	HI(<i>s</i> =0.1 V/s)	HI(<i>s</i> =0.01 V/s)
0	0.0180	0.0098	0.0090
0.2	0.0096	0.0089	0.0370
0.5	0.0067	0.0070	0.0096
1.0	0.0030	0.0020	0.014
2.5	0.2510	0.1672	0.1269
5.0	0.1052	0.0239	0.0034

换Pb²⁺后,钙钛矿晶体质量下降使得薄膜内部的离子易受到偏压诱导而发生迁移,从而导致严重的迟滞现象,这与文献报道离子迁移是造成异常迟滞现象的主要原因之一是一致的^[57,58]。我们猜测迁移的离子主要是卤素离子,因为高浓度的Cd²⁺替换,不仅使钙钛矿结晶质量变差,而且产生相分离析出PbI₂和MA₂CdI₄,可能导致钙钛矿中的卤素离子缺陷增多,使卤素离子在偏压下更容易发生迁移。

通过XRD, SEM, UV-Vis吸收和PL的表征结果证实,当Cd²⁺替换浓度为0.5%时不仅钙钛矿结晶质量和薄膜形貌有效改善,而且非辐射复合降低,光生载流子平均寿命提高,此时获得最优的器件性能而且无明显迟滞现象。

3 结论

本文通过不同浓度的Cd²⁺替换MAPbI₃钙钛矿薄膜中的Pb²⁺调控钙钛矿结晶性、薄膜形貌和光电特性,并研究其对于ITO/NiO_x/Cd-MAPbI₃/PCBM/Ag平面异质结钙钛矿太阳能电池性能和异常迟滞现象的影响。实

图 5 (网络版彩色) Cd^{2+} 替换 MAPbI_3 薄膜的 SKPM 表征. (a) 偏压诱导法 SKPM 测试原理图: 第一遍形貌扫描的同时在针尖上施加直流偏压 (V_{bias}), 第二遍表面电势扫描是将针尖抬高 10 nm 后沿着形貌曲线进行; (b) Cd^{2+} 替换浓度为 0% (c), 0.5% (d) 和 5.0% (e) 的 MAPbI_3 薄膜的平均表面电势随 V_{bias} 的变化趋势; (c)~(e) V_{bias} 分别为 -1, 0 和 1 V 时, 不同 Cd^{2+} 替换浓度 (0%, 0.5%, 5.0%) 的 MAPbI_3 钙钛矿薄膜的形貌图和表面电势图, 图中标尺为 500 nm

Figure 5 (Color online) Schematic illustration of SKPM measurement and SKPM characterization of Cd-incorporated MAPbI_3 films. (a) Schematic illustration of SKPM measurement: In the 1st pass, dc bias (V_{bias}) is applied during topography scan; In the 2nd pass for surface potential (SP) imaging, the tip is lifted up by 10 nm and scan on the basis of the topography line; (b) average surface potential of Cd-incorporated MAPbI_3 films measured by SKPM under different V_{bias} ; (c)~(e) topography and SP of Cd-incorporated MAPbI_3 with 0% (c), 0.5% (d), 5.0% (e) Cd^{2+} concentrations under -1, 0, 1 V bias voltages respectively. Scale bars are 500 nm

验结果证实, Cd^{2+} 替换浓度为 0%~0.5% 时可以有效地改善钙钛矿结晶质量和薄膜形貌, 降低非辐射复合提高荧光寿命, 实现器件能量转换效率从 15.38% 到 17.01% 的提升, 并且未出现显著的迟滞现象. 但是当 Cd^{2+} 替换浓度进一步从 1.0% 增加到 5.0% 时, 薄膜的结晶质量和形貌变差, 一方面出现相分离和孔洞抑制电荷传输, 另

一方面非辐射复合增加, 荧光寿命大大降低, 导致器件性能逐渐降低. 并且 Cd^{2+} 替换浓度超过 2.5% 时出现了严重的迟滞现象, 我们利用 SKPM 证实其与薄膜中的离子迁移有关. 我们的工作为金属离子替换钙钛矿光伏电池, 发光二极管和光探测器等方向的发展做出了有益的探索, 并为其未来的发展奠定了良好的基础.

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Summary for “金属离子替换的有机-无机钙钛矿太阳能电池及其迟滞现象”

Metal-substituted organic-inorganic perovskite photovoltaic device performance and hysteresis behavior

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Due to long carrier diffusion length, high defect tolerance and adjustable absorption spectra, organic-inorganic perovskite with chemical formula of ABX_3 ($A=CH_3NH_3$ (MA) or $HC(NH_2)_2$ (FA); $M=Pb$; $X=Cl, Br, I$) is one of the most promising candidates for low-cost solar energy harvesting. The power conversion efficiency (PCE) of the perovskite solar cells has experienced skyrocket increasing from 3.8% to over 23% in just 10 years after they showed up, which has already outperformed than that of multicrystalline Si. Based on *ab initio* calculation, it demonstrates that Pb^{2+} , taking part in bonding, is one of the most important factors that determines the crystallization, energy level, charge carrier dynamics as well as film morphology. Thus, a large number of metal ions have been reported to partial substitute Pb^{2+} , including isovalent substitution (Sn^{2+} , Sr^{2+} , Cd^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ba^{2+} , Zn^{2+} , Se^{2+} and Eu^{2+} , etc.) and anisovalent substitution (Cu^+ , Na^+ , Ag^+ , In^{3+} , Sb^{3+} , Al^{3+} and Bi^{3+} , etc.), which improved perovskite properties and device performance significantly. However, the effects of Pb^{2+} substitution on the anomalous hysteresis of perovskite solar cells have not been fully explored yet.

In this manuscript, isovalent Cd^{2+} substituted $MAPbI_3$ was employed as the model system, which excluded the interference of halogen ion defect formation if Pb^{2+} was substituted by isovalent metal ions. It is found that the crystallinity, morphology and photogenerated charge carrier dynamics of $MAPbI_3$ were tuned with different concentrations of Cd^{2+} . When the concentration of Cd^{2+} increased from 0% to 0.5%, the crystallinity and the morphology of perovskite films improved significantly, resulting suppressed non-radiative recombination and increased photogenerated charge carrier lifetime. The PCE of planar heterojunction photovoltaic devices with structure of $ITO/NiO_x/Cd-MAPbI_3/PCBM/Ag$ enhanced from 15.4% to 17.0%. Importantly, there is negligible hysteresis between forward and reverse current density-voltage ($J-V$) scan at different scan rate of 0.01, 0.1 and 1.0 V/s. By further increasing concentration of Cd^{2+} from 1.0% to 5.0%, the crystallinity of perovskite films deteriorated gradually, leading to higher non-radiative recombination and lower photogenerated charge carrier lifetime. The morphology of perovskite films also became worse, i.e., generated insulate phases and pin-holes, which prohibited charge transport. Even worse, incorporating high concentration of Cd^{2+} (2.5%–5.0%) not only deteriorated the device performance, but also led to serious hysteresis between forward and reverse $J-V$ scan. In order to further understand the hysteresis behavior under high concentration of Cd^{2+} , two-pass scanning Kelvin probe microscopy (SKPM) with additional DC bias (V_{bias}) applied in the first-pass topography scan have been employed. It is found that the average surface potential (SP) of the perovskite did not change with V_{bias} under Cd^{2+} concentration of 0% and 0.5%. Interestingly, the average SP of the perovskite changed significantly with V_{bias} under Cd^{2+} concentration of 5.0%, indicating significant ion migration and accumulation.

Our work provides a promising way to understand the device performance and hysteresis behavior in metal-substituted perovskite, which benefits the development of perovskite photovoltaic devices, light-emitting diodes, photodetectors etc. with metal ions engineering in future.

organic-inorganic perovskite solar cells, metal substitution, planar heterojunction, hysteresis, ion migration, scanning Kelvin probe microscopy

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