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论 文

基于$CuGa_2O_4$微米线光电探测器6×6阵列成像研究

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摘要 P型宽禁带半导体$CuGa_2O_4$的带隙约为4.4 eV, 吸收边位于280 nm左右, 使其可能成为制备全日盲紫外光电探测器的理想材料之一. 本研究利用化学气相沉积(CVD)法在蓝宝石衬底上制备出了厘米级长度的$CuGa_2O_4$微米线, 其长度可达0.8 cm, 直径约为35 μm. 基于生长的单根$CuGa_2O_4$微米线制备出了MSM型紫外光电探测器, 本研究表明, 在10 V偏压、280 nm紫外光照下, 器件表现出优异的光响应性能, 光暗电流比可达1.0×10^7, 以及高的响应度和比探测率, 其值分别为254.5 A/W和8.32×10^{15} Jones. 此外, 将36根$CuGa_2O_4$微米线转移到柔性聚对苯二甲酸乙二醇酯(PET)衬底上制备出6×6像素的紫外光电探测器阵列. 阵列展现出均匀的响应度, 其最大标准差约为0.84%. 在不同的弯折角度下(0°, 15°, 30°和45°)发现阵列器件的成像稳定, 能清晰地识别出“L”“N”“N”“U”字母的形状. 另外, 在弯折30°角度下对阵列进行了200次循环弯曲测试后, 器件的光电流值和暗电流值均未出现明显的衰减. 本文的研究结果为开发柔性全日盲紫外光电探测器阵列提供了一种可行的方法, 也体现了$CuGa_2O_4$材料在可穿戴式紫外监测与成像领域的应用前景.

关键词 化学气相沉积法, $CuGa_2O_4$微米线, 柔性紫外光电探测器, 阵列

PACS: 61.82.Fk, 72.40.+w, 81.15.Gh, 85.30.-z, 85.60.Gz

1 引言

紫外光电探测器是将紫外光信号转换为电信号, 从而实现对紫外光的检测和监测, 在无线通信、环境检测、导弹追踪、电子皮肤、仿生机器人等领域发挥着至关重要的作用[1–5]. 近年来, 紫外探测技术开始向柔性化、阵列化、成像化等方向发展[6]. 柔性探测器与传统光电探测器相比凭借可弯曲、便携、适配复杂曲面等特性, 在可穿戴设备、柔性传感系统等领域展现出巨大的应用潜力[7,8]. 例如, Kumar等人[9]制备出了基于Ga_2O_3/Cu_2O异质结的柔性透明紫外光电探测器, 该器件可阻挡近96%的紫外光. Li等人[10]采用射频磁控溅射方法, 在室温条件下在柔性的纸衬底上沉积ZnO薄膜, 并制备出MSM结构的光电探测器, 器件的响应率为0.86 A/W. 而探测器阵列化设计是通过集成多像素单元来实现紫外成像, 相比单一探测单元它更

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Shi J H, Feng Q J, Yao X Y, et al. Imaging research based on 6×6 $CuGa_2O_4$ microwire photodetectors array (in Chinese). Sci Sin-Phys Mech Astron, 2026, 56: 267313, doi: 10.1360/SSPMA-2026-0041

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能满足实际应用中对空间分辨能力的需求[11,12]. 目前, 超宽禁带半导体因其在特定波段的天然光吸收能力, 已成为制备日盲紫外光电探测器的核心材料[13]. 基于宽带隙Ga_2O_3, GaN和金刚石等材料的探测器阵列已有少量报道. 例如, Shen等人[14]采用金属有机化学气相沉积技术生长出了2英寸晶圆级氧化镓薄膜, 并制备出了8×8光电探测器阵列, 研究发现阵列中每个单元均表现出较高的性能和较快的响应速度, 其响应度为49.4 A/W, 比探测率为6.8×10^{14} Jones, 以及41 ms的响应时间. Xu等人[15]在硅晶片上制备了一个由GaN p-n同质结组成的光电探测器阵列, 阵列单元在0 V偏置电压下具有229.5 mA/W的响应度. Zhang等人[16]基于微波等离子体气相沉积(MPCVD)技术生长出了2英寸多晶金刚石, 在此基础上制备了可用于日盲成像的1×10像素光电探测器线性阵列, 研究发现探测器单元在228 nm紫外光照射时, 其响应率为45 mA/W.

金属氧化物半导体$CuGa_2O_4$具有约4.40 eV的禁带宽度, 理论上可覆盖220–280 nm的日盲紫外波段, 且具备优异的化学稳定性、热稳定性和催化活性等优点, 在开发日盲紫外探测器方面展现出潜在的材料优势[17–19]. 目前, $CuGa_2O_4$材料的研究多集中在光催化剂、气体检测、微波电介质、磁性材料等方面[20–23], 而在紫外探测器方面的研究还非常少, 只有本团队的2篇相关报道[24,25], 而基于该材料紫外光电探测器阵列成像方面的研究还未见报道. 本文利用CVD方法在蓝宝石衬底上生长出厘米级长度的$CuGa_2O_4$微米线, 通过激光光刻模版和电子束蒸发等方法, 基于36根$CuGa_2O_4$微米线制作出了6×6像素的柔性光电探测器阵列, 并对其紫外成像性能进行了研究.

2　实验和方法

2.1　$CuGa_2O_4$微米线生长

采用CVD法在蓝宝石衬底上生长$CuGa_2O_4$微米线. 首先将Ga_2O_3粉末(99.99%), Cu粉(99.99%)与作为还原剂的纳米碳粉(99.9%, 30 nm)按1:1:1.5的质量比均匀混合后作为反应源, 将其置于刚玉舟的中部, 清洗后的蓝宝石衬底则放于舟内反应源上方. 依次将石英盖片放置于刚玉舟上, 直至覆盖至舟出气口位置(图1). 然后通入流量为90 sccm的氩气作为载气, 以36℃/min的升温速率将生长室加热至1080℃后, 通入

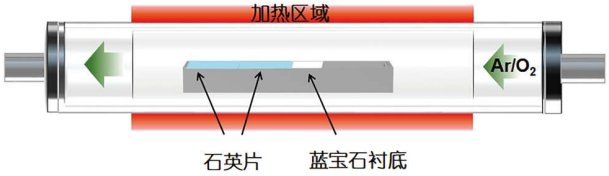


图 1　(网络版彩图) CVD实验装置图
Figure 1　(Color online) Schematic diagram of the CVD experimental system.

流量为70 sccm的氧气作为反应气体, 生长时间为30 min. 生长结束后, 系统冷却至室温取出样品.

采用数码相机、扫描电子显微镜(SEM)及能量色散X射线光谱(EDS), 对蓝宝石衬底上生长的$CuGa_2O_4$微米线的形貌、单根微米线的表面结构及其元素分布和组成进行了表征. 利用X射线衍射仪(XRD, Rigaku Ultima IV)分析了$CuGa_2O_4$微米线的晶体结构. 通过紫外-可见分光光度计测试了微米线在紫外至可见光范围内的光吸收特性.

2.2　6×6光电探测器阵列的制备

采用ICP-5100型感应耦合等离子体刻蚀机制作掩模版, 然后使用高真空电子束与热阻蒸发薄膜沉积系统(DZS500)在PET衬底上蒸镀图案化金电极, 其实物图如图2(a)所示. 从图中可见电极轮廓清晰, 无短路和黏连现象. 从蓝宝石衬底上剥离出36根长度和直径基本一致的单根$CuGa_2O_4$微米线并转移到图形化PET衬底上, 在微米线两端点涂银胶与金电极进行组装. 随后将器件置于60℃烘箱中固化15 min, 以确保电极与微米线间形成稳定的接触. 构建的$CuGa_2O_4$微米线柔性阵列的实物照片如图2(b)所示, 阵列长为33 mm, 宽19.5 mm. 利用Keithley 4200-SCS半导体参数分析系统, 在280, 308和365 nm三种波长紫外光照射下, 分别对器件的紫外探测特性进行了测试.

3　结果与讨论

3.1　$CuGa_2O_4$微米线的表征与分析

在样品生长的过程中, 发现随着刚玉舟上盖片数量的增加, $CuGa_2O_4$微米线的生长逐渐变长和密集, 这可能是由于盖片数量的增加, 刚玉舟内反应源气体流速逐渐变慢, 从而有利于原子的吸附和迁移, 促进了微米线的生长,已有相关报道[25]. 加盖两块石英盖片后

蓝宝石衬底上生长$CuGa_2O_4$微米线的实物照片如图3(a)所示. 可以看到, 在蓝宝石衬底上生长出了大量、高密度、透明的微米线, 长度最长可达0.8 cm. 图3(b)为单根$CuGa_2O_4$微米线的SEM图和元素分布图. 从图3(b)可见制备的$CuGa_2O_4$微米线表面非常光滑、边缘清晰、直径均匀约为35 μm. 此外, 还可看出Ga, Cu和O元素在微米线中分布均匀, 样品中Ga/Cu原子数之比为2.02, 接近2:1的理论化学计量比, 与$CuGa_2O_4$材料相符合.

图4(a)为微米线的XRD图谱, 图中除了位于41.67°的蓝宝石衬底(006)的衍射峰外, 其余衍射峰都和$CuGa_2O_4$标准卡片(JCPDS PDF#44-0183)相符合, 这说明生长的微米线为$CuGa_2O_4$. 图4(b)为$CuGa_2O_4$微米线在200–800 nm波长范围内的吸收光谱图. 由于$CuGa_2O_4$为直接带隙半导体, 其光学带隙可通过Tauc公式外推得到[26]:

$$(\alpha h\nu)^2 = A(h\nu - E_g). \tag{1}$$

其中, α是吸收系数, $h\nu$是入射光子的能量, A是材料系数. 可以获得样品的E_g约为4.40 eV, 对应的吸收边位于280 nm附近, 表明该材料可用于全日盲紫外光的探测.

3.2　单根$CuGa_2O_4$微米线紫外光电探测器的特性研究

图5(a)为单根$CuGa_2O_4$微米线光电探测器(阵列单元)在黑暗条件及不同波长(280, 308和365 nm)紫外光照射下的I-V特性曲线. 从图中可见, 在280 nm紫外光照射下, 器件产生的光电流明显大于308和365 nm波长下的光电流, 这表明器件对280 nm紫外光敏感. 此外, 阵列单元在280 nm紫外光和10 V电压时, 其光暗电流比可达1.0×10^7. 图5(b)为不同偏压下, 单个微米线单元的I-V特性曲线, 从图中可以看出器件光电流值随偏置电压的增加而增大, 这是由于电压增加导致器件内电场增强从而加速了光生载流子的迁移速度所引起[27].

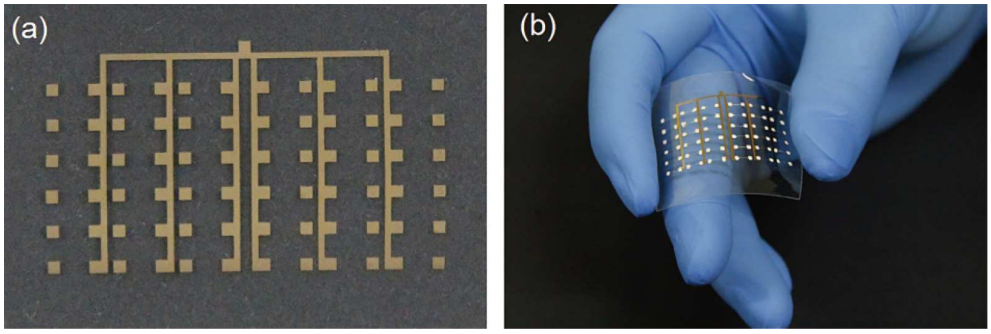


图 2　(网络版彩图) (a) 金电极的实物照片; (b) $CuGa_2O_4$微米线柔性阵列的实物照片
Figure 2　(Color online) (a) Photographs of gold electrode; (b) photographs of $CuGa_2O_4$ microwires flexible array.

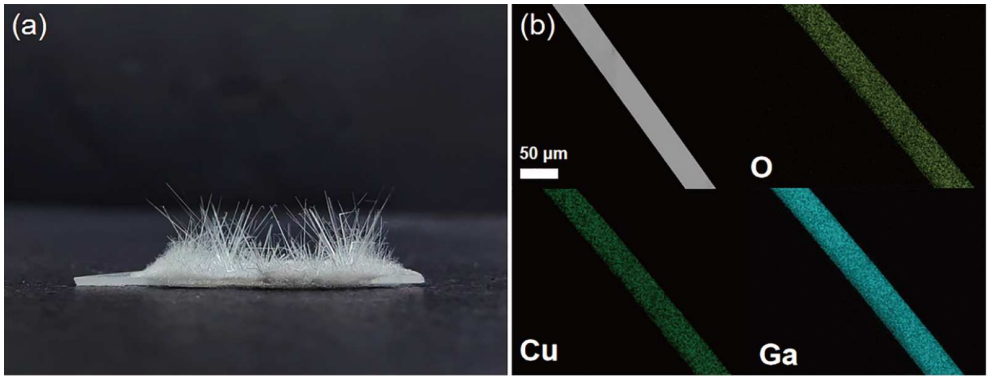


图 3　(网络版彩图) (a) 蓝宝石衬底上生长$CuGa_2O_4$微米线的相机照片; (b) 单根$CuGa_2O_4$微米线的扫描电子显微镜图像和O, Cu, Ga元素分布图
Figure 3　(Color online) (a) Photograph of $CuGa_2O_4$ microwires grown on sapphire substrate; (b) SEM image and distribution maps of O, Cu, and Ga elements in single $CuGa_2O_4$ microwire.

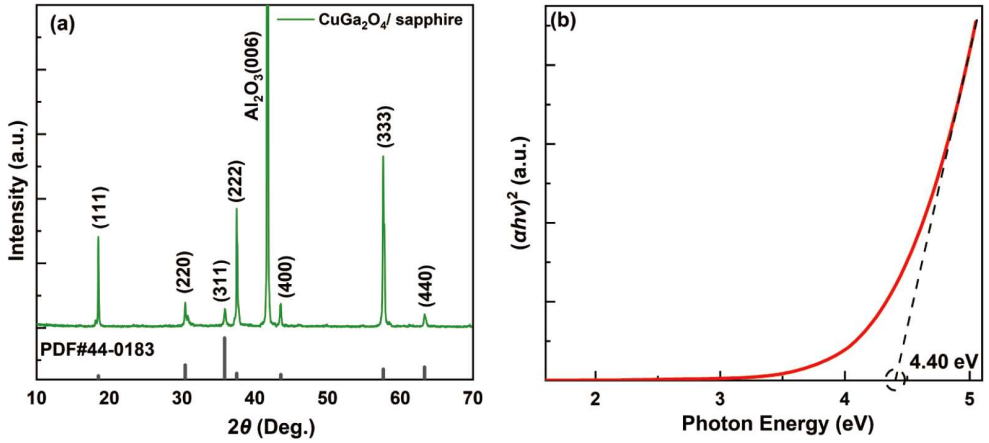


图 4　(网络版彩图) $CuGa_2O_4$微米线的晶体结构和光学表征. (a) XRD图; (b) 吸收光谱

Figure 4　(Color online) Structural and optical characterization of the $CuGa_2O_4$ microwires. (a) XRD pattern; (b) absorption spectrum.

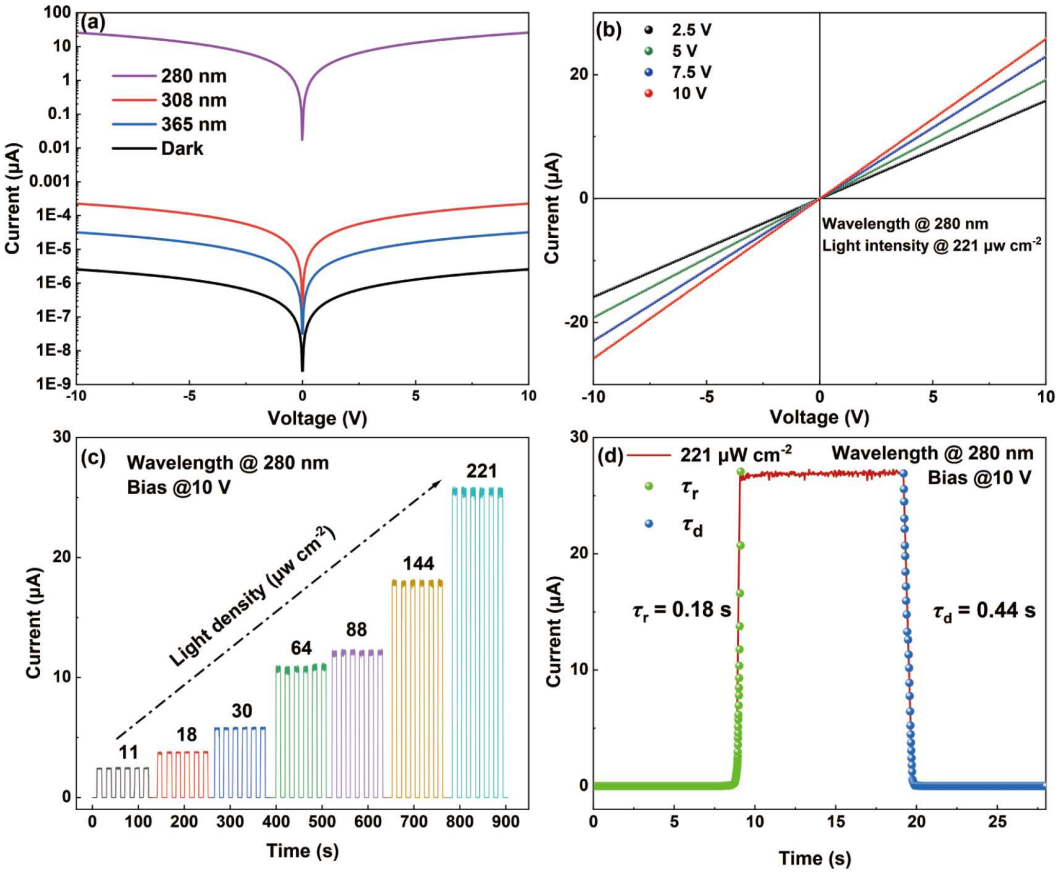


图 5　(网络版彩图) (a) 不同波长紫外光照和黑暗条件下, 器件的*I-V*特性曲线; (b) 不同偏压下器件的*I-V*特性曲线; (c) 不同光强下器件的*I-T*曲线; (d) 器件单个周期的*I-T*曲线

Figure 5　(Color online) (a) *I-V* characteristic curves of the device under UV light of different wavelengths and dark; (b) *I-V* characteristic curves of the device under different bias voltages; (c) *I-T* curves of the device under different light densities; (d) *I-T* curves of a single cycle of the device.

图5(c)为10 V偏压和不同光强下, 阵列单元的*I-T*图. 从图中可以看出器件的光电流随入射光强的增加而增大, 这是因为在280 nm紫外光照射下, 器件产生的电子-空穴对的数量会随光强的增大而增多所导致[28].

此外，还可看出在不同光强下光电探测器均表现出良好的重复性与响应稳定性. 为了评估器件的响应速度, 采用单e指数弛豫方程对其单个光响应周期曲线进行拟合, 结果见图5(d)所示, 其拟合公式定义为[29]:

$$I(t) = I_0 + A\mathrm{e}^{-t/\tau}. \tag{2}$$

其中, I_0为稳态光电流, A为拟合常数, t为时间, τ为弛豫时间常数. 上升时间(τ_r)是指光电流从10%上升到90%所需时间, 而下降时间(τ_d)是指光电流从90%下降到10%所需时间, 拟合得到τ_r为0.18 s, τ_d为0.44 s. 较快的响应速度为实现光电探测器阵列的紫外成像打下了坚实的基础.

为了评估阵列单元的日盲紫外探测性能，对器件的响应度(R)、外量子效率(EQE)、比探测率(D^*)和噪声等效功率(NEP)进行了计算. 响应度和EQE的定义分别为[30–32]:

$$R = \frac{I_{\mathrm{light}} - I_{\mathrm{dark}}}{PS}, \tag{3}$$

$$EQE = \frac{hcR}{q\lambda}, \tag{4}$$

$$D^* = \frac{R}{\sqrt{2qJ}}, \tag{5}$$

$$NEP = \frac{\sqrt{2qI_{\mathrm{dark}}}}{R}. \tag{6}$$

其中, I_{light}是光电流, I_{dark}是暗电流, P和S分别是入射光的光功率密度和光电探测器的有效光照面积. h是普朗克常数, c是光速, q为电子电量(1.6×10^{-19} C), λ是入射光的波长, R为光电探测器的响应度, J是暗电流密度. 图6为器件的响应度, EQE, D^*和NEP随光强的变化关系图像, 从图6(a)和(b)可以看出, 随着光强的减小, 紫外探测器件的响应度R和EQE逐渐增大. 光强与R和EQE之间的反比关系可归因于不同机制, 如载流子复合、吸收饱和及热效应[33]. 在高入射光强下, 光生载流子(电子-空穴对)浓度升高, 由于光强增加, 电子和空穴在参与光电流产生之前表现出更高的复合率, 从而减少了可用于光电流生成的载流子数量, 导致响应度降低[34]. 此外, 器件产生电子-空穴对的可用数量是有限的, 当光强较大时会饱和, 因此这种饱和效应减少

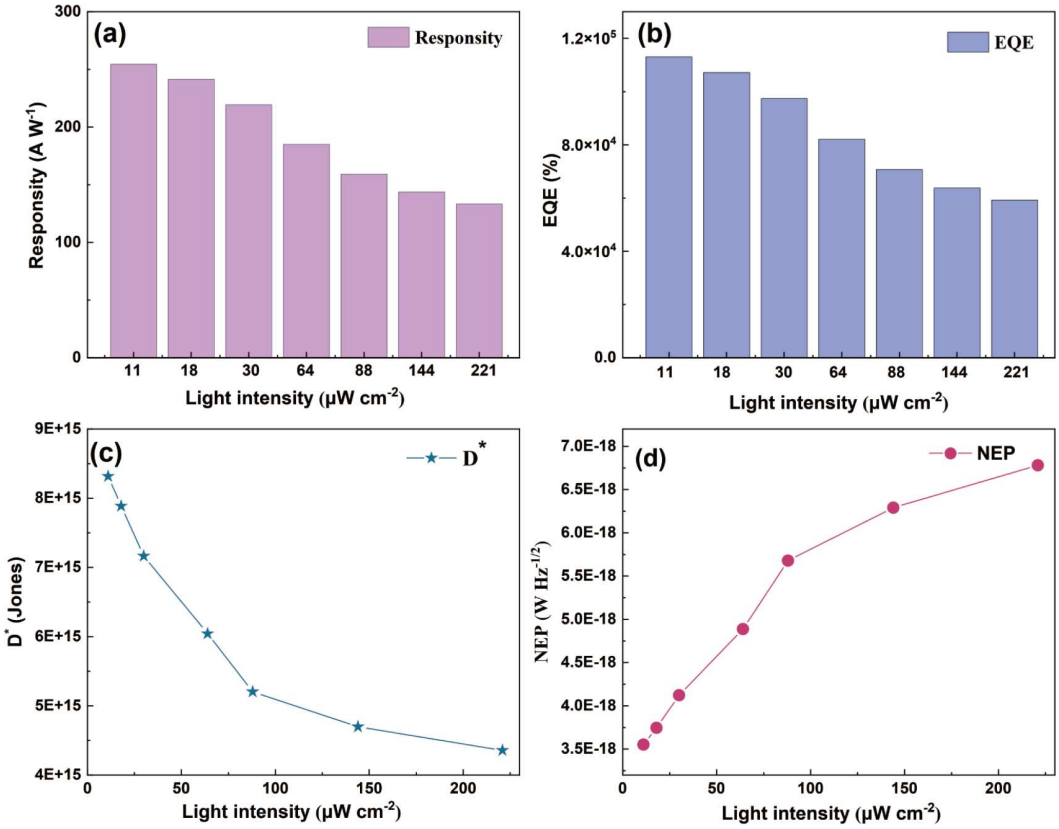


图 6　(网络版彩图)器件光电性能参数随光强的变化关系图像. (a) R; (b) EQE; (c) D^*; (d) NEP

Figure 6　(Color online) The plot of photoelectric performance parameters of the device versus light intensity (a) R; (b) EQE; (c) D^*; (d) NEP.

了吸收, 从而降低了响应. 另外, 过大的光强也会引入热效应, 增加非辐射复合, 降低载流子的迁移率, 进一步降低响应率和EQE[35]. 当光强为11 μW/cm^{2}时, 器件的响应度和EQE最大, 其值分别为254.5 A/W和112995%. 从图6(c)和(d)可以得出器件在光强为11 μW/cm^{2}时, 其最大比探测率D^*为8.32×10^{15} Jones, 最小NEP值为3.55×10^{-18} W/Hz$^{1/2}$.

3.3 基于$CuGa_2O_4$微米线光电探测器阵列的成像研究

图7(a)为6×6像素的$CuGa_2O_4$微米线紫外成像系统示意图. 阵列制备过程中, 由于生长或加工工艺等因素会降低阵列各像素单元的均匀性, 阵列中各像素单元的响应度、探测率等参数往往存在一定波动, 限制了其在集成化、高一致性应用场景中的性能. 微米线光电探测器阵列的关键优势在于其像素单元的可重构性. 通过独立更换单个像素中的微米线材料, 可以有效调控各像素的光电响应特性, 从而显著提升整个阵列的性能均匀性. 图7(b)和(c)是36个光电探测器单元在光强为221 μW/cm^{2}的280 nm光照下的光电流值和黑暗条件下的暗电流值及分别对应的二维映射图像. 阵列的最大标准差可由以下公式计算出[36]:

$$R_{\max}\ \mathrm{SD} = \frac{R_{\max} - R_{\mathrm{ave}}}{R_{\mathrm{ave}}}, \tag{7}$$

其中, $R_{\max}$和R_{ave}分别表示最大R和平均R, 通过计算得出所有阵列单元的最大标准差小于0.84%.

还对柔性光电探测器阵列在不同弯曲状态下的紫外成像性能进行了研究. 图8为阵列在不同弯折角度下的实物图片. 图9(a)–(d)为阵列在不同弯曲角度下(0°, 15°, 30°和45°)的成像结果, 从图中可以看到, 阵列可以清晰地识别出字母“L”“N”“N”“U”, 相较于传统刚性器件, 该柔性器件能够无缝贴合于复杂曲率表面, 而且发现其成像性能未出现显著衰减.

为进一步研究该柔性紫外光电探测器阵列在不同弯折次数下的机械稳定性, 还对器件在30°弯曲角度下, 进行了200次弯曲的循环测试, 结果如图10(a)和(b)所示. 在200次弯折后阵列各像素单元的光电流和暗电流没有表现出明显变化, 对机械形变的容忍度较大, 展现出了优良的光电性能稳定性.

表1为本文制备的器件与其他紫外光电探测器的

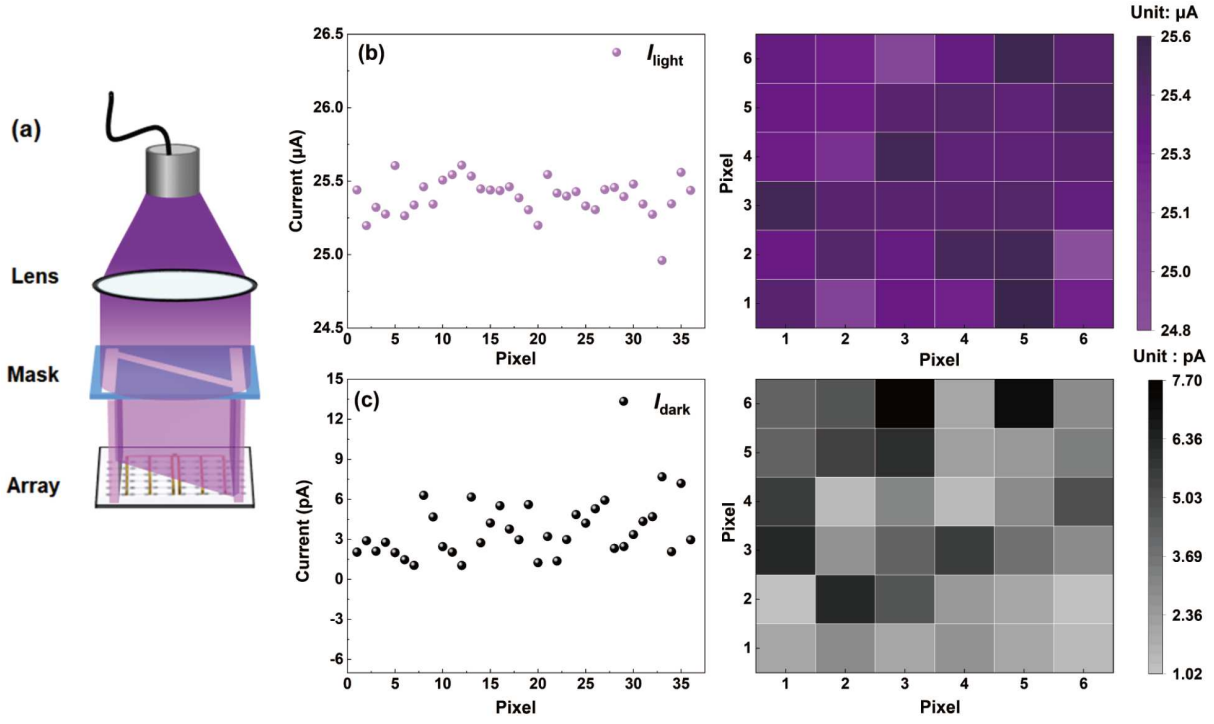


图 7　(网络版彩图) (a) 紫外成像系统示意图; 36个像素单元的电流及其二维映射图像. (b) 光电流; (c) 暗电流

Figure 7　(Color online) (a) Schematic photography of the UV imaging system; the current and two-dimensional mapping image of 36 pixels. (b) Photocurrent; (c) dark current.

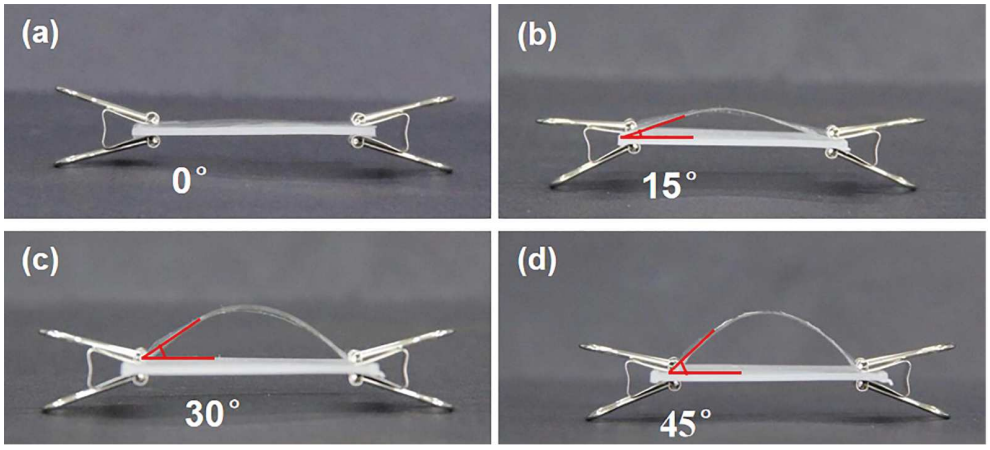


图 8　(网络版彩图)阵列在不同弯折角度下的实物图片. (a) 0°; (b) 15°; (c) 30°; (d) 45°
Figure 8　(Color online) Photographs of array at different bending angles. (a) 0°; (b) 15°; (c) 30°; (d) 45°.

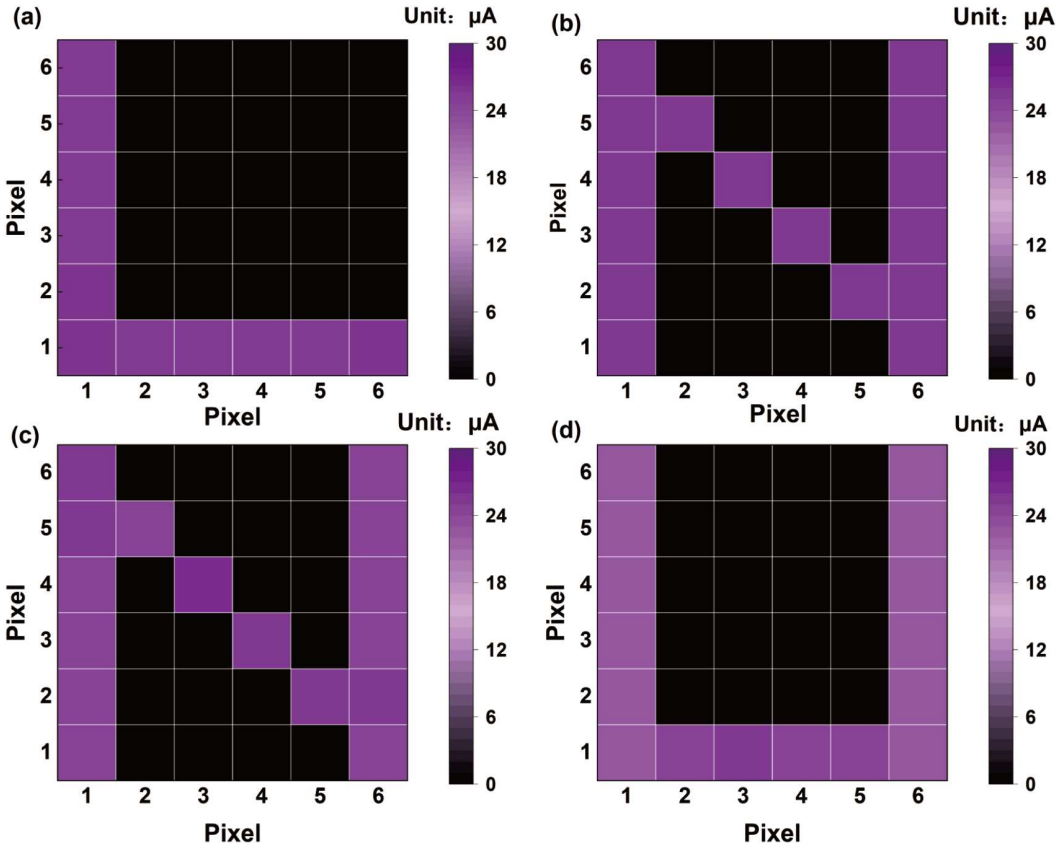


图 9　(网络版彩图)阵列在不同弯折角度下的电流分布图. (a) 0°; (b) 15°; (c) 30°; (d) 45°
Figure 9　(Color online) Current distribution of the array at different bending angles. (a) 0°; (b) 15°; (c) 30°; (d) 45°.

性能参数比较. 由此可见, 本研究制作的紫外光电探测器具有较高的响应度和比探测率, 并实现了紫外成像功能, 体现了$CuGa_2O_4$材料在柔性日盲紫外成像领域的重要应用潜力.

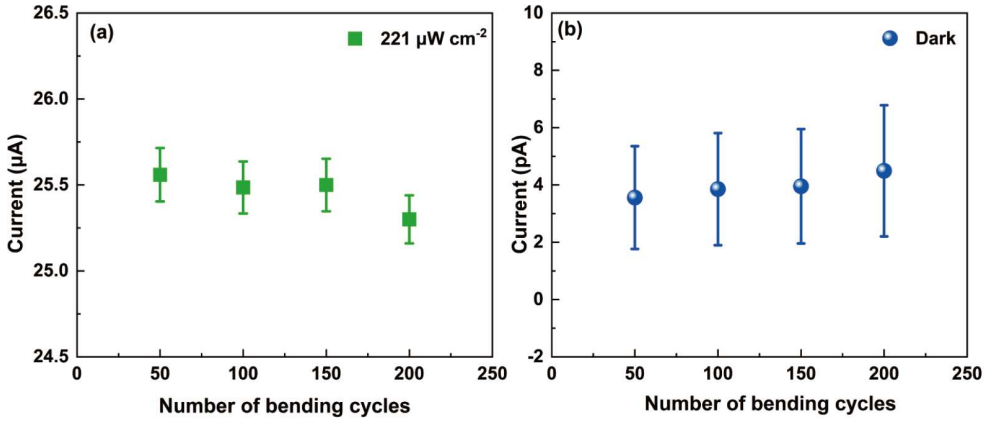


图 10　(网络版彩图)器件在不同循环次数弯折下电流的统计分布图. (a) 光电流; (b) 暗电流
Figure 10　(Color online) Statistical distribution of current under different cycles. (a) Photocurrent; (b) dark current.

表 1　与其他紫外光电探测器的性能比较
Table 1　Comparison of the performances of other UV photodetectors

Material	Flexible	*R*	*D**(Jones)	Response time	Array	Imaging	Ref.
β-Ga_2O_3	No	0.72 A/W	4.18×10^{11}	1.1/0.03 s	Yes	No	[37]
a-Ga_2O_3	Yes	222.98 A/W	2.0×10^{13}	0.43/0.4 s	Yes	Yes	[38]
GaN	No	4.23 A/W	1.76×10^{12}	45/22 ms	Yes	Yes	[39]
ZnO	Yes	5.0 mA/W	1.4×10^{9}	3.7/30.1 s	Yes	No	[40]
TiO_2	Yes	4.5 A/W	1.6×10^{11}	2.53/1.16 s	No	No	[41]
$CsCu_2I_3$	No	80 mA/W	2.7×10^{8}	640 μs/7.1 ms	Yes	Yes	[42]
SiC	Yes	55.89 A/W	1.22×10^{8}	12.5/9.5 s	No	No	[43]
$CuGa_2O_4$	Yes	254.5 A/W	8.32×10^{15}	0.18/0.44 s	Yes	Yes	This work

4　结论

采用CVD方法制备出了厘米级长度的$CuGa_2O_4$微米线, 其长度可达0.8 cm, 微米线的带隙值约为4.40 eV. 在10 V偏压和280 nm的紫外光照下, 单根$CuGa_2O_4$微米线光电探测器具有高达1.0×10^7的光暗电流比. 器件的响应度最大值为254.5 A/W, 比探测率为8.32×10^{15} Jones. 在此基础上将$CuGa_2O_4$微米线与PET衬底上的图案化金电极进行组装, 制作出6×6柔性紫外光电探测器阵列. 本研究发现, 光探测器阵列表现出均匀的光响应特性, 标准偏差约为0.84%. 此外, 阵列还表现出了优异的柔韧性, 在不同弯曲角度下均能够保持稳定成像, 并在多次弯折后未出现明显性能衰减. 本研究为开发$CuGa_2O_4$柔性光电集成器件提供了新思路, 推动了其在可穿戴紫外传感与成像领域的发展.

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Imaging research based on 6×6 $CuGa_2O_4$ microwire photodetectors array

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The band gap of P-type wide bandgap semiconductor $CuGa_2O_4$ is approximately 4.4 eV, and its absorption edge is around 280 nm, making it a potential ideal material for fabricating full-band solar-blind ultraviolet photodetectors. In this study, centimeter-sized $CuGa_2O_4$ microwires were fabricated on a sapphire substrate using the chemical vapor deposition (CVD) method. The length of microwires could reach up to 0.8 cm, and the diameter was approximately 35 μm. The metal-semiconductor-metal (MSM) ultraviolet photodetector was fabricated based on a single $CuGa_2O_4$ microwire. The device exhibits excellent photoresponse performance under 280 nm UV illumination, with a light-dark current ratio of up to 1.0×10^7, as well as high responsivity of 254.5 A/W and a specific detectivity of 8.32×10^{15} Jones. Furthermore, a flexible 6×6 UV photodetector array was fabricated by transferring 36 $CuGa_2O_4$ microwires onto a polyethylene terephthalate substrate (PET), and systematically investigated its imaging performance. The array demonstrated uniform responsivity, with a maximum standard deviation of about 0.84%. At different bending angles (0°, 15°, 30°, and 45°), the array maintained stable imaging and could clearly recognize the letters “L”, “N”, “N”, and “U”. In addition, after 200 bending cycle tests at 30°, both the photocurrent and dark current showed no significant degradation. These results demonstrate a feasible approach for developing flexible full-band solar-blind ultraviolet photodetector arrays and demonstrate the potential application of $CuGa_2O_4$ materials in wearable UV monitoring and imaging fields.

chemical vapor deposition, $CuGa_2O_4$ microwires, flexible ultraviolet photodetectors, array

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