主族层状低维半导体的偏振光探测器

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摘要 偏振探测在成像、遥感和生物检测等领域具有非常广泛的应用. 为了契合光电领域高度集成化的发展目标, 偏振光探测器的器件结构需要跳出复杂的检偏器与探测器分离式结构模型, 开发新型探测路线. 对偏振光天然敏感的主族层状低维半导体可实现直接偏振光探测, 实现探测结构的简化. 基于Ⅳ族锗系和锡系的低对称性层状半导体在短波近红外具有较高的光响应以及偏振灵敏度, 并且基于二维GeSe的偏振光探测器已经实现对近红外实物的二维式扫描偏振成像. 基于Ⅴ族锑系和铋系的层状半导体在可见光波段具有较宽的光谱响应以及低的探测噪声, 也已实现偏振成像. 基于该两类主族层状低维半导体的偏振成像为未来偏振图像传感技术提供了一种简洁可行的思路.

关键词 主族元素, 低维半导体, 偏振光探测器, 偏振成像

随着对信息器件功能的要求不断提升, 研究者正在逐步开发新的半导体体系. 2004年, Novoselov等人^[1]通过机械剥离的方法制备出原子层厚度的石墨烯, 该石墨烯展现出较高的载流子迁移率以及较强的双极性场效应特性, 由此开启了二维材料的研究热潮. 二维材料层内以较强的共价键结合, 层间以弱的范德华力相结合. 虽然石墨烯具有超高的迁移率($10^6 \text{ cm}^{-1} \text{ V}^{-1}$)^[2], 但是零带隙的能带结构限制了其在半导体领域的应用. 尽管研究者通过外延生长石墨烯或者对双层石墨烯进行双栅调控的手段成功打开了石墨烯的带隙^[3,4], 但有限的带隙打开程度使得半导体领域的研究者不得不将目光转移至其他二维半导体材料. 以MoS₂为代表的二维过渡金属族硫属化合物(transition metal chalcogenides, TMDs)以其优异的半导体特性成为近些年的研究热点, 在微电子领域具有潜在的应用价值, 有望成为延续摩尔定律的重要选项之一^[5-9]. 除此之外, 二维六方

氮化硼也被广泛用于二维材料的衬底以及器件介电层, 大大提升了二维材料及其器件的电学性能^[10-12]. 近年来, 一些二维过渡金属碳化物和氮化物在电化学储能等领域也表现出巨大的优势^[13,14]. 除了上述由过渡族金属和主族元素组成的二维半导体外, 近几年低维材料尤其是二维材料领域的研究者注意到一些新型的层状主族半导体, 即由Ⅳ族、Ⅴ族、Ⅵ族和Ⅶ族元素组成的化合物半导体. 区别于核心的主族半导体组成元素在元素周期表中根据Ⅳ族呈对称性分布, 如以Si为代表的Ⅳ族及 $A^{8-N}B^N$ 型的Ⅲ-Ⅴ族化合物半导体(A、B代表Ⅲ族元素和Ⅴ族元素, N代表Ⅴ族元素的价电子数), 组成这类新型的主族层状半导体的化学元素在元素周期表中根据Ⅳ族呈现非对称性分布. 核心半导体互补的外层电子结构使得晶体内部呈现完美匹配的共价键, 配位数为4, 促使核心主族半导体晶体内部具有非常强的力学稳定性和三维空间对称性. 区别于此, 非

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对称分布的主族半导体外层电子的非互补性导致化学键的复杂度增大, 进一步导致原胞内原子组成的复杂性, 如GeSe, 一个原胞内具有8个原子, 原胞体积高达 $196.6 \text{ \AA}^3$ ^[15]. 这种原子以及化学键的复杂性导致晶体的对称性元素较少, 从而表现出电学和光学上的各向异性, 尤其是对线偏振光具有天然的敏感性, 这一特性优于核心主族半导体, 并有望跳出现存复杂偏振成像系统设计思路而开拓一种新型偏振光探测技术. 同时, 该类半导体表现为层状, 层间结合力为较弱的范德华力, 很容易制备成二维结构, 在柔性光电器件领域具有潜在的应用价值. 魏钟鸣课题组聚焦该类低维主族层状半导体, 具体包括锗系和锡系的IV-V/VI族半导体(GeSe、GeSe₂、GeAs、Sn₂S₃和SnS)^[15-21], 以及铋系和铊系的V-VI/VII族半导体(Sb₂S₃、Bi₂S₃、SbI₃和Sb₂-(S_{0.33}Se_{0.67})₃)^[22-25], 探索其光电各向异性以及在偏振光探测领域的应用, 并拓展至偏振成像领域.

1 基于IV族锗系和锡系的层状半导体偏振光探测

理论研究表明, 以GeSe和SnS为代表的单硫属IV族化合物具有非常稳定的单层力学稳定性, 并具有非常强的可见光吸收系数和较大的载流子迁移率, 是继过渡金属族硫属化合物以来又一极具应用前景的新型二维材料, 被广泛应用于太阳能电池、光催化以及忆阻器等光电及存储领域^[26-33]. 同时, 该类材料又具有较低的晶体对称性和强的面内各向异性. 偏振光探测及偏振成像作为光电领域重要的分支, 亟须具有强光电各向异性和强光学吸收的半导体. 单硫属IV族化合物同时具备该两大特点, 对偏振光天然敏感, 非常适于制备成新型的简洁偏振光探测器, 相较于目前偏振探测领域复杂的光学元件系统更具优势. 魏钟鸣课题组^[15,19]探索了该类单硫属IV族化合物的面内各向异性以及偏振光探测性能. 在此基础上, 研究了双硫属IV族化合物的GeSe₂以拓展其偏振光谱响应至紫外波段^[16], 并研究了锗系IV-V族化合物二维GeAs的偏振特性, 发现了二向色性以及偏振特性在光谱上的垂直翻转现象^[17].

制备二维IV族锗系和锡系层状半导体的方法为: 先通过化学气相传输法(chemical vapor transport, CVT)合成块体材料, 再通过机械剥离法得到其二维结构. 如二维GeSe的CVT合成, 首先, 将高纯度的GeSe粉末密封在真空度为 10^{-5} Torr(1 Torr=133.322 Pa)的石英管中, 再将石英管置于双温区管式炉中. 温区1为反应区(640°C),

温区2为合成区(450°C), 两者相距20 cm. GeSe粉末位于温区1的位置, 在此温度下保持10 h, 期间高温反应区内的GeSe粉末会升华并传输到低温合成区合成GeSe晶体. 然后, 将两个温区温度置换, 温区1降至400°C, 温区2升至700°C并保持10 h. 通过反复置换温区使得石英管内尽可能多地合成高质量GeSe晶体, 最终慢速冷却至350°C后, 再自然冷却至室温^[15].

如图1所示, 5种半导体材料皆表现为层状结构, 即面内以共价键结合而面外为弱的范德华力结合, 该化学键特性使得材料很容易制备成二维材料. GeSe和SnS都属于正交晶系, 相对于核心半导体的立方晶系和六方晶系, 该类半导体在面内存在两个特殊的轴, 如图1(b), (f)中的“扶手椅”(armchair)方向和“之字形”(zigzag)方向, 两个方向具有非常明显的光学特性^[34]. GeSe在晶体的“扶手椅”方向相较于“之字形”方向表现出更强的光学吸收, 因此对不同方向的线偏振光具有不同的吸收. 如图2(a)所示, 插图为测试用的GeSe纳米片, 随着入射线偏振光的角度变化, GeSe表现出不同的吸收. GeSe₂和GeAs属于单斜晶系, 相对于前两者表现出更为明显的晶体低对称性以及面内光学各向异性. 材料对线偏振光的光学吸收各向异性称为线性二向色性(linear dichroism, LD), 通常将材料对不同偏振角的入射光吸收系数最大值与最小值的比值称为二向色比值, 是描述材料光学各向异性的最直观的物理量之一, 被经常用于描述双折射晶体、分子光吸收特性以及光学元件的特征值^[35-37]. GeSe和SnS在近红外波段都具有最好的二向色性, 分别对808与862 nm具有3.02和3.06的最高线性二向色比值^[15,19]. 而GeSe₂由于较宽的带隙(2.96 eV), 对具有2~5 eV的光子都具有强的吸收, 在405 nm处具有1.2的线性二向色比值^[16]. 从理论上分析半导体能带导带底以及价带顶跃迁 Γ 点位置的波函数, 可以揭示这一光学跃迁各向异性, 即晶体的非对称性导致波函数沿着两个方向的分布不同, 具有镜面对称性的一组波函数分布导致该方向上的光学跃迁积分为零, 而另一方向非零^[20].

除了研究二维材料在吸收光谱中所表现的二向色性以外, 研究者还通过角分辨的拉曼光谱、方位角依赖的反射差分谱以及偏振光学显微镜来表征材料的结构与光学各向异性^[38-40]. 如正交晶系GeSe的A_g拉曼模振动强度, 在平行和交叉两种偏振图景中表现出非等强度分布的四瓣状, 而B_{3g}拉曼模式振动表现出等强度的四叶状, 这种强度分布与GeSe晶体的对称性息息相

图 1 IV族锗系和锡系层状半导体的原子排列图。(a) 基于IV族锗系和锡系的层状半导体在元素周期表中的分布；(b) 正交晶系的GeSe晶体沿着 a 轴层状分布， c 轴为扶手椅方向^[15] (Copyright 2017, American Chemical Society)；(c) 单斜晶系的GeSe₂晶体沿着 c 轴方向层状分布， a 轴为扶手椅方向^[16] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim)；(d) 单斜晶系的GeAs晶体沿着 c 轴层状分布， a - b 面内原子排列具有各向异性^[17] (Copyright 2018, American Chemical Society)；(e) 具有混合价态电子结构的层状正交Sn₂S₃晶体的原子排列^[18] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim)；(f) 正交晶系的SnS沿着 c 轴层状分布， a - b 面内具有各向异性^[34] (Copyright 2019, American Chemical Society)

Figure 1 Atomic arrangement of layered semiconductors based on Group IV germanium and tin systems. (a) Distribution of layered semiconductors based on Group IV germanium systems and tin systems in the periodic table of elements; (b) the orthorhombic GeSe is distributed in layers along the a -axis, and the c -axis is the armchair direction^[15] (Copyright 2017, American Chemical Society); (c) the monoclinic GeSe₂ is distributed in layers along the c -axis direction, and the a -axis is the armchair direction^[16] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim); (d) the monoclinic GeAs is distributed in layers along the c -axis, and atoms in the a - b plane are anisotropic^[17] (Copyright 2018, American Chemical Society); (e) atomic arrangement of layered orthorhombic Sn₂S₃ with the mixed-valence electronic structure^[18] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim); (f) the orthorhombic SnS is layered along the c -axis and anisotropic in the a - b plane^[34] (Copyright 2019, American Chemical Society)

关，可以通过四叶状的强度分布来无损地表征非规则形貌的二维材料晶向^[15]。又如GeSe₂，可以通过偏振光学显微镜清晰地观察到，随着光源偏振角的变化，材料呈现不同的颜色，这一特征表明GeSe₂具有明显的双折射现象以及反射各向异性。综上种种光学测试手段，从不同程度上反映了材料内部的结构各向异性以及光跃迁的光学各向异性。

强的偏振光吸收各向异性使得锗系和锡系的层状半导体具有天然的偏振光敏感性，如果作为光探测器的感光层，能够识别入射光的偏振特性，可大大简化偏振光探测系统，有望取代现阶段复杂的偏振成像系统。图2(b)为基于二维GeSe的偏振光探测器，整个偏振光探测过程如下：一束光经过起偏器成为线偏振光，在其后增加一个对应波长的半波片，旋转半波片来改变入射光的偏振角，通过测试经过探测器两端的源漏电流来研究器件的偏振特性。图2(c)展示了GeSe偏振光探测器在不同源漏电压调控下对不同偏振角的808 nm入射光的光响应。波浪状的等高线图揭示了强的光响应

各向异性。偏振光探测器对于偏振光的敏感程度可以用各向异性光电流比值或者各向异性比来表征。各向异性比(anisotropy ratio)可通过公式 $(I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$ 计算得到，即描述光电流之间的相对差异，越接近于1表示各向异性越强，越接近于0表示各向同性越强^[41,42]。相对于前者描述，各向异性光电流比值或称为偏振灵敏度 $I_{\max} / I_{\min}$ ，即测试最大光电流与最小光电流的比值，更为直观^[43~49]。如图2(d)~(f)所示，GeSe、GeAs和GeSe₂均表现出了明显的光电流各向异性，GeSe和GeAs在近红外都具有非常高的光电流各向异性，如GeSe在808 nm处 $I_{\max} / I_{\min}$ 为2.16，这与吸收测试的二向色比值接近。尽管吸收测试显示GeAs在近红外只有1.42的吸收二向色比值，但基于GeAs的偏振光探测器在830 nm处具有高达4.4的各向异性光电流比值，这得益于器件的肖特基势垒^[17]。因此，建立肖特基势垒或者异质结形式的偏振光探测器是提高偏振光探测器性能的重要手段^[21,46,47]。如图2(f)所示，GeSe₂在紫外波段(405和266 nm)展现了较好的光电流各向异性，突破了

图 2 锗系和锡系半导体的光电各向异性测试。(a) 不同偏振角入射光下GeSe纳米片的吸收光谱^[15] (Copyright 2017, American Chemical Society); (b) 二维GeSe偏振光探测器器件示意图^[15]; (c) 二维GeSe偏振光探测器的光电流与漏极电压和入射偏振光(808 nm)的关系^[15]; (d) 2 V漏极电压下, GeSe偏振光探测器光电流与偏振角的关系^[15]; (e) GeAs偏振光探测器的垂直翻转现象^[17] (Copyright 2018, American Chemical Society); (f) GeSe₂偏振光探测器在蓝光及紫外波段的光电流与偏振角关系^[16] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim)

Figure 2 Measurements of photoelectric anisotropy of germanium and tin systems semiconductors. (a) Absorption spectra of the GeSe nanosheet under incident light with different polarization angles^[15] (Copyright 2017, American Chemical Society); (b) schematic diagram of two-dimensional GeSe polarization-sensitive photodetector^[15]; (c) the relationship of photocurrent of two-dimensional GeSe polarization-sensitive photodetectors with drain voltage and incident light (808 nm)^[15]; (d) the relationship between photocurrent and polarization angle of GeSe polarization-sensitive photodetectors under 2 V drain voltage^[15]; (e) perpendicular optical reversal of GeAs polarization-sensitive photodetectors^[17] (Copyright 2018, American Chemical Society); (f) the relationship between the GeSe₂ polarization-sensitive photodetector photocurrent and the polarization angle of the incident blue and ultraviolet light^[16] (Copyright 2019, WILEY & VCH Verlag GmbH & Co. KGaA, Weinheim)

二维半导体偏振光探测波长的短波极限。

2 基于V族锑系和铋系的层状半导体偏振光探测

随着二维材料在偏振光探测中展现的优势, 研究者再次关注到一些一维以及准一维的层状半导体材料, 发展其在偏振光探测领域的应用^[22-25,50,51]。位于V族的锑系和铋系硫属化合物具有宽的光谱响应、卓越的热电性能以及新奇的拓扑现象^[52-54]。同时, 这一系列半导体具有正交和单斜的低对称晶体结构, 如图3(b), (c)所示。正交晶系的Sb₂S₃和Bi₂S₃在某一晶向上具有较短的化学键与周期性, 表现为沿着某方向层状堆叠且在层内具有链状的一维结构, 易于形成纳米线或者纳米带的形貌, 具有非常明显的光电各向异性。

合成高质量V族锑系和铋系的层状半导体主要有物理气相沉积(physical vapor deposition, PVD)与化学气相沉积(chemical vapor deposition, CVD)两种方法。如

Sb₂S₃纳米线的PVD合成, 高纯的硫化锑粉末位于管式炉的中游高温区(580°C), 上游放置高纯硫粉作为辅助, 下游放置二氧化硅衬底, 管式炉中通以15 sccm流速的高纯氩气, 2 min后缓慢降至室温, 在氧化硅衬底上合成Sb₂S₃纳米线。Sb-S-Se合金纳米线则利用单质硫粉、硒粉和锑粉作为前驱体, 通过CVD方法合成。

魏钟鸣课题组^[22,23]发展了基于Sb₂S₃的宽光谱偏振光探测和基于Bi₂S₃的低噪声偏振光探测。如图4(a)所示, 基于Sb₂S₃纳米线的偏振光探测器在360~1550 nm波段都具有较好的光谱响应, 并在整个可见波段内都具有较高的各向异性光电流比值, 尤其是在638 nm波段具有2.54的高各向异性光电流比值。类似于GeAs探测器中的肖特基结增强各向异性原理, Au和Sb₂S₃之间形成的肖特基结也在一定程度上增强了各向异性^[22]。基于Bi₂S₃纳米线的偏振光探测器实现了宽光谱、高开关比以及低噪声的偏振光探测。Hooge参量是描述1/f噪声随着电流以及频率倒数变化的一个系数:

图3 V族锑系和铋系层状半导体的原子排列图。(a) 基于V族锑系和铋系的层状半导体在元素周期表中的分布；(b) 正交晶系的 Sb_2S_3 晶体的原子沿着 a 轴层状分布， b - c 面内具有各向异性^[22](Copyright 2020, Wiley-VCH GmbH)；(c) 正交晶系的 Bi_2S_3 晶体的原子沿着 c 轴方向层状分布， a - b 面内具有各向异性^[23]；(d) 三方晶系的 SbI_3 晶体的原子沿着 a 轴层状分布^[24](Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)；(e) 正交晶系 $\text{Sb}_2(\text{Se}_{0.33}\text{S}_{0.67})_3$ 的原子排列^[25](Copyright 2021, IEEE)

Figure 3 Atomic arrangement of layered semiconductors based on Group V antimony and bismuth systems. (a) Distribution of layered semiconductors based on Group V antimony and bismuth series in the periodic table; (b) the atoms of the orthorhombic Sb_2S_3 crystal are layered along the a -axis, and there exists anisotropy in the b - c plane^[22] (Copyright 2020, Wiley-VCH GmbH); (c) the atoms of the orthorhombic Bi_2S_3 crystal are distributed in layers along the c -axis direction, and there is anisotropy in the a - b plane^[23]; (d) the atoms of the trigonal SbI_3 crystal are distributed in layers along the a -axis^[24] (Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (e) atomic arrangement of orthorhombic $\text{Sb}_2(\text{Se}_{0.33}\text{S}_{0.67})_3$ ^[25] (Copyright 2021, IEEE)

$$\frac{S_I}{I^2} = \frac{\alpha_H}{fN}, \quad (1)$$

其中， S_I 代表噪声频谱， I 代表电流， f 代表频率， N 代表载流子密度， α_H 为Hooge参量，数值越小，代表器件的噪声越小^[55]。如图4(b)所示，相较于其余一维探测器， Bi_2S_3 探测器具有较低的噪声，Hooge参量接近于 10^{-5} ^[23]。

除了肖特基结增强偏振探测的各向异性性能以外，魏钟鸣课题组^[24]发展了另一种提高偏振探测性能的方案：纳米核壳结构 $\text{SbI}_3/\text{Sb}_2\text{O}_3$ 。核壳结构的制备方法如下：首先，通过CVT方法合成 SbI_3 晶体，将作为前驱体的锑粉和碘颗粒按照1:3的摩尔比例混合均匀，并添加少许碲粉作为催化剂共同密封在 10^{-5} Torr的真空石英瓶中。瓶中前驱体粉末位于双温区管式炉的高温反应区(600°C)，瓶的另一端位于双温区管式炉的低温合成区(450°C)，高温保持72 h后，以1°C/h的速率冷却至

300°C，再自然冷却至室温。通过机械剥离的方法将 SbI_3 晶体剥离成薄层并转移至二氧化硅衬底上，在氩气环境下50°C退火1 h后，在室温空气中自组装形成 $\text{SbI}_3/\text{Sb}_2\text{O}_3$ 核壳结构。如图3(d)所示，三方晶系的 SbI_3 在面内具有一定的低对称性，通过测试偏振光探测，在450 nm处具有一定的各向异性光电流比。然而，通过自组装的方法，在 SbI_3 纳米线周围包覆一层各向同性的立方晶系 Sb_2O_3 壳层，形成核壳纳米线结构(图4(d))，最终各向异性光电流比提高至3.14。该方案通过核壳形式建立异质结降低内核材料 SbI_3 的对称性，从而提升偏振光探测性能，与其他研究者通过建立面内范德华异质结或者二维材料和体材料相结合的异质结形式来提高偏振探测性能具有相同的作用^[47]。

同时，魏钟鸣课题组^[25]通过合金化的手段发展了宽光谱 $\text{Sb}_2(\text{Se}_{0.33}\text{S}_{0.67})_3$ 偏振光探测器。以高纯度锑粉、硫粉以及硒粉为前驱体，通过CVD方法合成 Sb-S-Se 合

图 4 基于V族锑系和铋系层状半导体的偏振探测。(a) 基于 Sb_2S_3 的偏振光探测器在整个可见光波段具有较好的响应度(黑色虚线)以及高各向异性光电流比(红色虚线)^[22](Copyright 2020, Wiley-VCH GmbH); (b) 基于 Bi_2S_3 的宽光谱偏振光探测器具有低的噪声(Hooge参数量接近 10^{-5})^[23]; (c) 通过合金化手段制备 $\text{Sb}_2(\text{Se}_{1-x}\text{S}_x)_3$ 合金半导体提升偏振探测性能(x 代表S和Se元素中S的百分比)^[25](Copyright 2021, IEEE); (d) 通过核壳纳米线结构降低核层半导体的对称性^[24](Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

Figure 4 Polarization-sensitive photodetection based on layered semiconductors of Group V antimony and bismuth systems. (a) The Sb_2S_3 -based polarization-sensitive photodetector exhibits wide photo response in the whole visible light (black dotted line) and high anisotropic photocurrent ratio (red dotted line)^[22] (Copyright 2020, Wiley-VCH GmbH); (b) the Bi_2S_3 -based broad-spectrum polarization-sensitive photodetector shows low noise with the Hooge parameter as low as nearly 10^{-5} ^[23]; (c) the alloy semiconductor $\text{Sb}_2(\text{Se}_{1-x}\text{S}_x)_3$ improves the polarization-sensitive photodetection performance (x represents the percentage of S in S and Se elements)^[25] (Copyright 2021, IEEE); (d) symmetry-reduction of the core semiconductor through the core-shell nanowire structure^[24] (Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

金纳米线, 硫粉和硒粉位于上游低温区($100\sim 250^\circ\text{C}$), 锑粉位于中游高温区($620\sim 640^\circ\text{C}$), 氧化硅衬底位于下游低温区($400\sim 500^\circ\text{C}$)。通过控制前驱体的摩尔比例来合成不同比例的Sb-S-Se合金半导体。如图4(c)所示, 通过调整合金中Se和S的比例, 在整个波长范围内将偏振光探测性能调整到最佳, 图中颜色代表将不同波长以及不同化学计量比下的各向异性光电流比进行归一化, 可见合金半导体中硫占1/3时, 探测器对532 nm的偏振光最为敏感。相较于 Sb_2S_3 偏振光探测器, $\text{Sb}_2(\text{Se}_{0.33}\text{S}_{0.67})_3$ 偏振光探测器具有更高的响应度和探测率, 并有效地提升了近红外以及紫外区域的偏振光探测性能。

3 基于主族层状低维半导体的偏振成像

主族层状半导体在偏振光探测领域表现出非凡的性能, 非常有望成为下一代偏振成像系统的基础单元。与现有的偏振成像技术中检偏器和探测器分离式结构不同, 该类偏振光探测器可以直接识别偏振光的方向。为进一步探索其在偏振成像领域的应用, 魏钟鸣课题

组分别以 GeSe ^[20]、 Sb_2S_3 ^[22]和 Bi_2S_3 ^[23]为像元进行红外以及可见光波段的偏振成像。

该二维成像系统仅需要一个像元便可实现清晰成像。如图5(a)所示, 左图为实物图, 右图为以 Bi_2S_3 探测器为像元进行二维扫描式成像, 结果非常清晰地呈现了实物的细节^[23]。此二维扫描成像系统主要包括可调焦式透镜组、集成电路信息采集组、电动旋转台以及电脑主机和显示器。探测器位于透镜组之后的集成电路上, 通过调整探测器的位置使探测器位于透镜焦面上, 通过电动旋转台控制探测器在焦平面上水平和竖直两个方向上二维式扫描并采集实物的光学信息, 最终转化成灰度值上传至电脑显示器中。基于此二维扫描成像系统以及具有偏振敏感性的独立偏振光探测器像元, 对于入射的偏振实物图像, 仅需要改变入射偏振光方向与材料晶体特征轴之间的夹角, 便可呈现不同的成像结果, 以此实现对实物图的偏振成像。 Bi_2S_3 探测器和 Sb_2S_3 探测器都可作为偏振成像系统的像元实现偏振成像。以 Sb_2S_3 探测器为例, 如图5(b)所示, 基于 Sb_2S_3 探测

图5 基于主族层状半导体的偏振成像。(a) 以Bi₂S₃探测器为像元的成像系统成像结果: 左图为实物, 右图为成像结果^[23]; (b) 以Sb₂S₃探测器为像元对镂空实物“UCAS”的可见光偏振成像结果(UCAS为中国科学院大学的英文首字母)^[22] (Copyright 2020, Wiley-VCH GmbH); (c) 以GeSe探测器为像元对偏振U形热发光管进行近红外偏振成像, 将具有不同偏振角(0°~90°)的U形管的成像结果按照灰度值的高度分布绘制^[20]

Figure 5 Polarization imaging based on main group layered semiconductors. (a) Imaging results of the imaging system with Bi₂S₃ photodetectors: The left picture is the object, and the right picture is the imaging result^[23]; (b) the visible light polarization imaging results of the hollow object “UCAS” with the Sb₂S₃ photodetector (UCAS is the English acronym of the University of Chinese Academy of Sciences)^[22] (Copyright 2020, Wiley-VCH GmbH); (c) the near-infrared polarization imaging of the polarized U-shaped thermoluminescent tube is performed with the GeSe photodetector, and the imaging results of the U-shaped tube with different polarization angles (0°~90°) are drawn according to the height distribution of gray values^[20]

器的偏振成像结果显示, 该探测器像元对具有不同偏振角的“UCAS”实物具有不同的成像结果。为了更为明显地表现不同角度下的成像结果差异, 采用各个角度下的成像结果减去90°下的成像结果, 因此90°的成像结果并未表现出来^[22]。该“UCAS”实物为一白光实物, 证明Sb₂S₃探测器可以很好地应用于可见光区域的偏振成像。与Sb₂S₃宽的可见光响应波段不同, 二维GeSe半导体的光响应波段更接近于近红外区域。如图5(c)所示, GeSe探测器可以作为近红外偏振成像的像元, 实现对808 nm波长的发热U形红外灯管的偏振成像, 结果非常高辨识度地展示了U形灯管的偏振角为0°^[20]。这一单像元扫描式成像探索证实了主族层状低维半导体可以用于偏振图像传感器, 为未来开发新型偏振成像技术提供了思想。

4 结论与展望

基于IV族锗系和锡系的单硫属化合物半导体GeSe与SnS在短波近红外波段具有强的光响应各向异性, 尤其是二维GeSe半导体, 在近红外偏振光探测以及偏振

成像领域展现出巨大的优势; 基于V族铋系与锑系的层状半导体偏振探测器展现出宽波段和低噪声的优势, 尤其是在可见光波段具有优异的偏振灵敏度。除此之外, 还发展了肖特基型探测器、核壳纳米线探测器以及合金化技术手段, 成功提高了偏振探测性能; 基于GeSe、Sb₂S₃以及Bi₂S₃的单像元二维扫描偏振成像实验已经成功证实了对实物偏振成像的可行性。尽管如此, 基于单探测器的二维扫描成像距离目前的商用成像仍有很大差距, 主要原因在于, 与体半导体材料相比, 二维材料(少数层)的探测率较低以及集成化相对困难。因此, 基于该类半导体的高性能图像传感器集成化是未来发展的重要方向。诸如石墨烯、MoS₂和MoTe₂的二维材料目前都已实现了大尺寸晶圆级制备^[56~59], 可借鉴此技术合成大尺寸晶圆级二维GeSe, 并通过图形化实现GeSe探测器的集成化; 基于铋系和锑系的V族化合物层状半导体易于制备成纳米线及纳米带的形貌, 可以借鉴碳纳米管的定向排列成膜思路^[60], 合成大面积的单向排列V族铋系和锑系纳米线阵列, 并通过图形化技术实现集成化。

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Summary for “主族层状低维半导体的偏振光探测器”

Polarization-sensitive photodetectors based on main group layered low-dimensional semiconductors

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Polarization-sensitive photodetection is widely used in imaging, remote sensing, and biological detection. In order to meet the development goal of high integration in the photoelectric field, the polarization-sensitive photodetector structure needs to jump out of the complex structure model of separating polarizer and detector and develop a new detection route. The main group layered low-dimensional semiconductors, which are naturally sensitive to polarized light, can realize directly polarization-sensitive photodetection and simplify the detection structure. Here we summarize some polarization-sensitive photodetectors based on main group layered low-dimensional semiconductors, point out the shortcomings and give suggestions for future development. Low-symmetry layered semiconductors based on Group IV germanium and tin systems have high optical response and polarization sensitivity in short-wave near-infrared. At 808 nm, GeSe has a dichroic ratio of 3.02 and an anisotropic photocurrent ratio of 2.16. In particular, the polarization-sensitive photodetector based on two-dimensional GeSe has realized two-dimensional scanning polarization imaging of near-infrared objects. The GeSe-based photodetector can identify the U-shaped heat pipe's polarization angle with a high degree of recognition. In addition, we also prepared a GeSe₂-based polarization-sensitive photodetector to extend the detection range to the ultraviolet band. The GeAs-based photovoltaic polarization-sensitive photodetector with low absorption dichroic ratio (1.42) has high anisotropic photocurrent ratio (4.4) under near-infrared range, which reveals the importance of the Schottky junction. The polarization-sensitive photodetection based on IV group layered 2D semiconductors inspired us to investigate the polarization-sensitive photodetection based on some V group layered 1D semiconductors. Such semiconductors are mainly composed of antimony and bismuth-based nanowires based on Group V. The constituent elements of these semiconductors are mainly antimony, bismuth of Group V, Group VI and Group VII elements. The phenomenon of easy growth into nanowires reveals to some extent the low symmetry of the crystal structure of this type of semiconductor. Layered semiconductors based on Group V antimony and bismuth usually have wide spectral response and low detection noise in the visible band, and polarization imaging has also been realized. All these confirm the feasibility of polarization-sensitive photodetection and imaging in the visible region for V group layered 1D semiconductors. In addition, polarization-sensitive photodetectors with a core-shell structure (SbI₃/Sb₂O₃) and alloying techniques (Sb₂(Se_{0.33}S_{0.67})₃) have been developed, both of which enhance the polarization-sensitive photodetection performance. An isotropic cubic Sb₂O₃ shell is coated around the anisotropic trigonal SbI₃ nanowire by self-assembly, forming a core-shell nanowire structure. The established heterojunction between core and shell successfully reduces the symmetry of SbI₃, thus improving the detection performance of polarized light. For the second option, we have prepared a Sb₂(Se_{0.33}S_{0.67})₃-based polarization-sensitive photodetector with wide spectral response through alloying technology. By adjusting the ratio of Se and S, the polarization-sensitive photodetection performance is adjusted to the best in the whole wavelength range. Compared with Sb₂S₃-based polarization-sensitive photodetectors, Sb₂(Se_{0.33}S_{0.67})₃-based polarization-sensitive photodetectors have higher response and detection rate, and effectively improve the polarization-sensitive photodetection performance in near-infrared and ultraviolet regions. Therefore, layered low-dimensional semiconductors based on Group IV (germanium and tin systems) and Group V (antimony and bismuth systems) show potential application in the field of polarization-sensitive photodetection and polarization imaging, which provides a simple and feasible idea for polarization image sensing technology in the future.

main group elements, low-dimensional semiconductors, polarization-sensitive photodetector, polarization imaging

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