二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的制备及其光电探测性能

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摘要 $\text{In}_{2/3}\text{PSe}_3$ 因其对称性破缺的晶体结构、良好的发光性质和直接带隙特性,在光电子器件领域具有巨大的应用潜力.本研究采用化学气相输运法合成了 $\text{In}_{2/3}\text{PSe}_3$ 单晶并通过机械剥离方法获得了二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片.借助二次谐波(second-harmonic generation, SHG)和光致发光(photoluminescence, PL)光谱对其非线性光学和发光性质进行了系统的研究,结果表明 $\text{In}_{2/3}\text{PSe}_3$ 纳米片具有本征对称性破缺的晶体结构和优异的发光性质.通过微纳加工技术构筑了基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器并研究了其光探测性能.基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器在365 nm波长的光照下,具有极低的暗电流(25 fA)、优异的探测度(6.28×10^{11} Jones)、高的开关比(4×10^4)以及超快的响应速度(14 μs /24 μs).这些优异的光电性能预示着 $\text{In}_{2/3}\text{PSe}_3$ 有潜力成为新一代高性能光探测器的核心材料.

关键词 二维材料, $\text{In}_{2/3}\text{PSe}_3$, 直接带隙, 非线性光学, 光学器件

二维层状半导体材料因其具有原子级的厚度、较强的光与物质相互作用和易于规模化集成等优点,现已成为电子和光电子领域的研究热点之一^[1~5].近年来,一类新兴的二维层状半导体材料——金属磷硫属化合物(metal phosphorus trichalcogenides, MPTs)因其新颖的电学和光学特性而受到广泛的关注^[6~8].MPTs是由金属阳离子与 $[\text{P}_2\text{S}_6]^{4-}$ 或 $[\text{P}_2\text{Se}_6]^{4-}$ 构成,金属元素和原子比例的多样性变化赋予了MPTs更多的自由度^[9].相较于过渡金属硫属化合物, MPTs的能带间隙覆盖了1.3~3.5 eV^[10],有着更好的光吸收效率和丰富的电子能带结构,在光电子领域有着广阔的应用前景.

$\text{In}_{2/3}\text{PSe}_3$ 是MPTs家族中的一种具有特殊结构的材料.不同于其他MPTs材料层内金属离子填充 $[\text{P}_2\text{Se}_6]^{4-}$ 骨架的结构特点, $\text{In}_{2/3}\text{PSe}_3$ 中层内的金属原子位点2/3被铟原子占据,1/3由空位占据,层间则是由范德瓦尔斯力连接,堆垛形式为ABC,独特的晶体结构赋

予 $\text{In}_{2/3}\text{PSe}_3$ 对称性破缺的特点^[11],使其具有成为非线性光学材料的潜力.块体 $\text{In}_{2/3}\text{PSe}_3$ 是一种直接带隙半导体(E_g 约为2.0 eV)^[12,13],直接带隙材料中的电子跃迁不需要声子的辅助,因此 $\text{In}_{2/3}\text{PSe}_3$ 对光的利用效率更高,更加凸显了其在光电子器件领域的巨大优势^[14].然而目前鲜有关于二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片光电性质的报道,因此对二维 $\text{In}_{2/3}\text{PSe}_3$ 的光学和光电性质的研究具有十分重要的意义.

本研究通过化学气相输运的方法合成了高质量的 $\text{In}_{2/3}\text{PSe}_3$ 单晶,采用机械剥离的方法获得了二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片.借助二次谐波和光致发光光谱对 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光学性质进行了系统的研究,二次谐波光谱的结果证明 $\text{In}_{2/3}\text{PSe}_3$ 纳米片具有对称性破缺的晶体结构.光致发光光谱的结果表明 $\text{In}_{2/3}\text{PSe}_3$ 纳米片具有良好的发光特性和较长的荧光寿命.通过微纳加工技术构筑了基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器并研究了

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其光探测性能. 基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光电探测器件展现出了优异的光响应特性和超快的响应速度, 在电子和光电子领域有着广阔的应用前景.

1 实验

(i) 材料合成. 本实验采用化学气相输运方法合成了高质量的 $\text{In}_{2/3}\text{PSe}_3$ 单晶. 将铟粉(In, 纯度99.99%, Innochem)、磷粉(P, 纯度99.9%, Alfa)和硒粉(Se, 纯度99.9%, Aladdin)按照化学计量比研磨混合, 在真空下(10^{-3} Torr, 1 Torr $\approx$ 133 Pa)使用火焰枪将原料与输运剂碘(I_2 , 纯度99.5%, Acros)一同封装进石英玻璃管内. 将石英管放置在水平双温区管式炉内, 其中高温区温度为923 K, 低温区温度为873 K, 保温50 h后经30 h缓慢冷却至室温, 获得黑色的 $\text{In}_{2/3}\text{PSe}_3$ 单晶. 采用机械剥离的方法用胶带将单晶反复剥离, 将黏附有材料的胶带贴合到硅片(300 nm SiO_2)上, 撕开胶带后在衬底上得到二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片.

(ii) 材料表征. 本实验借助X射线衍射仪(X-ray diffractometer, XRD D2 PHASER, Bruker)和透射电子显微镜(transmission electron microscope, TEM Tecnai G2 F20, FEI)对 $\text{In}_{2/3}\text{PSe}_3$ 的结构进行表征; 借助光学显微镜(optical microscope, OM BX53M, Olympus)和原

子力显微镜(atomic force microscope, AFM Dimension Icon, Bruker)对二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的形貌和厚度进行表征; 借助激光共聚焦拉曼光谱仪(Raman Alpha 300 RS+, WITec)和飞秒激光器(Verdi, Coherent)对二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的拉曼光谱、光致发光和二次谐波性质进行研究.

(iii) 光探测器件的制备和测试. 通过电子束曝光(Quantum FEG 650, FEI和ELPHY Plus, Raith GmbH)、显影、镀膜、去胶的方法构筑基于二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的两电极器件, 镀膜采用高真空镀膜仪(Nexdep, Angstrom Engineering), 蒸镀电极为Cr/Au(10/90 nm). 将制备好的器件置于探针台(TTPX, Lakeshore)中, 借助半导体分析仪(4200SCS, Keithley)和365 nm激光(DC2200, Thorlabs)对器件的光电性能进行测试.

2 结果与讨论

2.1 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的晶体结构、合成及表征

$\text{In}_{2/3}\text{PSe}_3$ 属于三方晶系, $R\bar{3}$ 空间群(No. 146), 晶格参数为 $a=b=6.362$ Å, $c=19.929$ Å. 图1(a)是 $\text{In}_{2/3}\text{PSe}_3$ 晶体的结构示意图. $\text{In}_{2/3}\text{PSe}_3$ 是一种层状材料, 在二维平面内以强的化学键连接, 而层与层之间则是由弱的范德

图1 二维 $\text{In}_{2/3}\text{PSe}_3$ 的晶体结构及表征. (a) $\text{In}_{2/3}\text{PSe}_3$ 晶体的结构示意图; (b) 块体 $\text{In}_{2/3}\text{PSe}_3$ 晶体的XRD图谱; (c, d) 机械剥离的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光学显微镜(OM)照片及对应的原子力显微镜(AFM)照片; (e) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的拉曼光谱

Figure 1 Structure and characterizations of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets. (a) Crystal structure of $\text{In}_{2/3}\text{PSe}_3$; (b) XRD pattern of $\text{In}_{2/3}\text{PSe}_3$ crystal; (c, d) OM image and corresponding AFM image of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets; (e) Raman spectra of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets

瓦尔斯力相结合,层间距为0.67 nm.沿 c 轴看去,围绕磷原子的金属离子形成类似石墨烯的蜂窝状结构.在一层中,硒原子的排列顺序为六方最密堆积,而金属阳离子和哑铃型的P-P二聚体则填充在八面体的空隙中^[15].常见MPTs的元素比例一般为1:1:3,金属阳离子为+2价,而 $\text{In}_{2/3}\text{PSe}_3$ 中的金属原子位点上存在本征的晶体空位,铟离子和晶体空位的统计学比例为2:1,这使其成为该族材料中唯一具有+3价单一阳离子的结构^[16].此外,相较于大多数MPTs, $\text{In}_{2/3}\text{PSe}_3$ 层内的P-P原子的间距较大(2.22 Å),使得磷原子几乎与硒原子层处于同一平面^[12].因此, $\text{In}_{2/3}\text{PSe}_3$ 的每一层可以看作是由中间的 In^{3+} 和空位与上下两层 $[\text{PSe}_3]^{2-}$ 形成的三明治结构组成的.图S1(a)是借助化学气相输运方法合成 $\text{In}_{2/3}\text{PSe}_3$ 单晶的示意图,得到的 $\text{In}_{2/3}\text{PSe}_3$ 单晶的尺寸普遍约为2 mm × 2 mm (图S1(b)),表面为黑色,具有金属光泽.为了进一步确定物相,对获得的单晶进行了XRD测试,单晶的衍射峰尖锐明显,且与标准卡片(PDF#77-0791)一致,证明我们合成的 $\text{In}_{2/3}\text{PSe}_3$ 单晶具有非常高的结晶质量.通过机械剥离的方法在300 nm SiO_2/Si 衬底上获得了少层 $\text{In}_{2/3}\text{PSe}_3$ 纳米片,图1(c)和(d)分别是少层 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光学显微镜照片和对应的原子力显微镜照片.可以看出, $\text{In}_{2/3}\text{PSe}_3$ 纳米片展现出明显的层状特性,最薄处的厚度为3.7 nm(5个原子层的厚度).为了获得 $\text{In}_{2/3}\text{PSe}_3$ 纳米片

更详细的物相信息^[17],我们借助共聚焦拉曼光谱仪对 $\text{In}_{2/3}\text{PSe}_3$ 纳米片进行表征.图1(e)为 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的拉曼光谱,共有5个拉曼峰,其中93.0和153.5 cm^{-1} 的峰对应于面外振动模 A_g , 77.9、167.1和217.9 cm^{-1} 的峰对应于面内振动模 E_g (峰位归属判断见图S2)^[17].一般来说,位于低波数(低于100 cm^{-1})的拉曼峰源于金属原子的振动,而高波数的拉曼峰则源于P-P、P-Se键的振动^[18],铟原子的拉曼振动峰信号明显强于其他常见的金属磷硒化合物^[18,19],可作为特异性区分 $\text{In}_{2/3}\text{PSe}_3$ 与其同类型材料的重要指标.

透射电子显微镜是分析材料微观结构的有效工具.图2(a)是剥离得到的二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的低倍透射照片,纳米片的高透光度表明其具有较薄的厚度.图2(b)是纳米片的高分辨透射照片,图中所示的两个晶面间距均为0.33 nm,晶面夹角为60°,分别对应于(300)和(030)晶面.其对应的选区电子衍射图像呈现出六方对称的单晶衍射花样,衍射斑点清晰,与{300}晶面族对应,说明通过机械剥离所获得的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的单晶特性和高结晶性.图2(d)~(f)是对 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的边缘进行元素面分布扫描,可以看到, In、P和Se三种元素在整个样品中分布均匀,且3种元素的原子比例接近2:3:9(图S3).透射电子显微镜数据的结果表明我们获得了高质量的单晶 $\text{In}_{2/3}\text{PSe}_3$ 纳米片.

图2 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的透射电子显微镜(TEM)表征. (a) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的低倍透射照片; (b, c) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的高分辨透射照片及对应的选区电子衍射图像; (d~f) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的元素面分布扫描照片

Figure 2 TEM characterization of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets. (a) Low magnification TEM image of $\text{In}_{2/3}\text{PSe}_3$ nanosheets; (b, c) high-resolution TEM image and corresponding selected electron diffraction image of $\text{In}_{2/3}\text{PSe}_3$ nanosheets; (d~f) element mapping of $\text{In}_{2/3}\text{PSe}_3$ nanosheets

2.2 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光学性质研究

二次谐波产生(second harmonic generation, SHG)效应与晶体结构的对称性、取向和缺陷有着密切的关系,已被广泛地应用于材料科学、催化和生物工程等领域的前沿研究中^[20]。当激光照射到非线性材料表面时,如图3(a)所示,不仅会产生与入射光相同波长的光,还会产生波长为1/2的光(倍频光),即为二次谐波效应^[21]。 $\text{In}_{2/3}\text{PSe}_3$ 属于非心空间群 $R\bar{3}$ 。对称性的破缺使其具有成为非线性光学材料的潜力。图3(b)展示了在760~960 nm波长的激发光下, $\text{In}_{2/3}\text{PSe}_3$ 的SHG信号强度随激发光波长的变化规律,由图中可知 $\text{In}_{2/3}\text{PSe}_3$ 纳米片在800 nm的激发光下具有最强的SHG信号,因此我们选择在800 nm激发光波长下进行进一步测试。图3(c)是功率依赖的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的SHG光谱,峰位位于400 nm的峰恰好对应于800 nm激发光的SHG信号。提取不同功率下的SHG信号强度,在对数坐标下经过拟合可得,SHG的信号强度与激发光功率强度的平方成正比(图3(d)),拟合后的斜率值为2.01。该结果与电偶极子理论所得的计算值2是一致的^[22,23]。图S4的SHG强度面扫

描图结果显示测试的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片具有良好的均一性,均匀的强度证明剥离的纳米片为纯相且有着均匀的厚度。针对 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的非线性光学性质的研究表明, $\text{In}_{2/3}\text{PSe}_3$ 对称性破缺的结构能够产生本征的二次谐波效应,具有成为一种新的非线性光学材料的潜力。

由于二维材料具有非常大的比表面积,材料内部的一些杂质和缺陷可能会影响其电子结构和光学性质,因此本实验借助光致发光光谱研究二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光学性质及其对应的内部缺陷结构^[24]。图4(a)展示了室温下不同厚度 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光致发光光谱。在532 nm波长的激发光下, $\text{In}_{2/3}\text{PSe}_3$ 纳米片在600~700 nm的范围内出现了明显的光致发光峰(峰位在650 nm左右),与此前报道的 $\text{In}_{2/3}\text{PSe}_3$ 单晶的带隙基本吻合^[13],光致发光光谱的结果表明在室温下 $\text{In}_{2/3}\text{PSe}_3$ 纳米片具有非常好的发光特性。图4(b)给出了 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的发光峰位与其厚度的变化关系,可以看出在20 nm以上,纳米片的带隙随厚度变化基本不变;而在20 nm以下,随着纳米片厚度的减小,材料的带隙有显著的增加,这种变化主要是源自二维纳米片的量子尺寸效应^[25]。温度依赖的光致发光光谱有助于提供更多的有关其发光

图3 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的非线性光学性质。(a) SHG测试原理图; (b) SHG信号强度随激发光波长在760~960 nm的变化规律; (c) 800 nm激发光波长下功率依赖的SHG光谱; (d) SHG信号强度与激发光功率的关系

Figure 3 Nonlinear optical characterization of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets. (a) Schematic illustration of SHG measurement; (b) excitation wavelength-dependent SHG measurements from 760 to 960 nm; (c) power-dependent SHG measurements under 800 nm; (d) power-dependent SHG intensity

图4 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光致发光光谱表征. (a) 不同厚度纳米片的光致发光光谱. (b) 发光峰位随材料厚度的变化关系. (c) 温度依赖的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光致发光光谱(80~300 K); 插图: 发光带隙随温度的变化关系. (d) 功率依赖的 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光致发光光谱. (e) 发光峰位随激光功率的变化关系. (f) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的荧光寿命曲线

Figure 4 PL spectra of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets. (a) PL spectra of $\text{In}_{2/3}\text{PSe}_3$ nanosheets with different layers. (b) Layer-dependent PL peak position. (c) Temperature-dependent PL spectra ranging from 80 to 300 K. Inset: Temperature-dependent PL peak energy. (d) PL spectra at different laser power intensities. (e) Power-dependent PL intensity. (f) PL decay of $\text{In}_{2/3}\text{PSe}_3$ nanosheets

机制和内部结构的信息. 图4(c)展示了80~300 K的光致发光光谱, 光谱左侧(约630 nm)尖锐且非常强的发光峰为 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的带边发射峰(near-band-edge, NBE). 除此之外, 在光谱右侧(720 nm左右)有1个较弱的宽峰, 且随着温度的上升其峰强急剧下降, 低温下出现的较弱宽峰类似于一些III-V族半导体中出现的表面施主-受主对(donor-acceptor-pair, DAP)峰^[26], 当温度升高时, 施主和受主俘获的载子会离化, 因而这种DAP发光峰只能在低温下观察到. 随着温度的升高, 由于不断增强的电子-声子相互作用和晶格的热膨胀^[27], $\text{In}_{2/3}\text{PSe}_3$ 纳米片的NBE发光峰的峰强逐渐降低, 且发光峰的位置出现了明显的红移, 带隙从2.0 eV降低到1.84 eV. 带隙值随温度的变化可以通过Varshni公式进行拟合^[28]:

$$E(T) = E(0) - \alpha T^2 / (T + \beta), \quad (1)$$

其中, $E(0)$ 是在0 K时的带隙, α 表示高温时的变化系数, T 为温度, β 为低温时的二次变分系数. 经过拟合后可得到 $E(0)$ 为2.05 eV, α 为0.86 meV/K, 这一结果与根据块体变温吸收测试得到的温度系数(0.85 meV/K)基本相同. 为了进一步明确 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的发光机制, 我们测试了不同激发光功率下的PL光谱(图4(d)), 发光峰的强度

随功率的变化关系可以在对数坐标下通过公式 $I-L^k$ (I 代表发光强度, L 代表功率密度, k 代表拟合系数)拟合^[29]. 如图4(e)所示, 得到的拟合系数 k 为1.25, 这一数值对应的跃迁机制为类激子跃迁^[30,31]. 荧光寿命光谱是理解载流子动力学行为的有效手段, $\text{In}_{2/3}\text{PSe}_3$ 纳米片的荧光寿命约为240 ps(图4(f))^[32], 该数值要略高于一些常见的二维材料^[33,34], 较长的荧光寿命会导致载流子的复合效率变慢, 有利于更多载流子的分离. $\text{In}_{2/3}\text{PSe}_3$ 纳米片直接带隙的特点、类激子的跃迁机制和较长的荧光寿命使其在光电子器件领域有着广阔的应用前景.

2.3 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光电性能研究

为了研究 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光电性能, 我们构筑了基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的两电极器件(图5(a)), 纳米片的厚度为25 nm(图S5). 根据 $\text{In}_{2/3}\text{PSe}_3$ 纳米片(厚度为16 nm)的紫外-可见吸收光谱(图5(b))可以看出, $\text{In}_{2/3}\text{PSe}_3$ 纳米片的吸收峰主要在300~400 nm的近紫外区, 吸收峰的边缘在600 nm左右, 按照直接带隙拟合公式:

$$\alpha h\nu = A(h\nu - E_g)^m, \quad (2)$$

图 5 二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光电探测性能研究. (a) 基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器的示意图. (b) $\text{In}_{2/3}\text{PSe}_3$ 纳米片的紫外-可见吸收光谱; 插图: 拟合指数 m 为0.5时得到的光学带隙. (c) 波长依赖的光响应曲线. (d) 入射光波长为365 nm时功率依赖的电流-电压(I - V)曲线. (e) 不同功率下的电流-时间(I - t)曲线. (f) 光电流与入射光功率的关系. (g) 光响应循环稳定性 I - t 曲线. 光探测器的上升时间(h)和下降时间(i)

Figure 5 Optoelectrical property of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheet. (a) Schematic view of the device based on $\text{In}_{2/3}\text{PSe}_3$ nanosheet. (b) UV-vis optical absorption spectrum of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheet. Inset: Fitting optical bandgap when $m=0.5$. (c) Wavelength-dependent photoresponse curve. (d) Power-dependent I - V curves under 365 nm illumination. (e) I - t curves under different light intensities. (f) Fitting curve between photocurrent and light intensity. (g) Time-resolved photoresponse I - t curves of the photodetector. Rising time (h) and decay time (i) of the photodetector

其中, α 是吸收系数, h 是普朗克常量, ν 是光的频率, m 在直接带隙的条件下取值为0.5^[35,36], 拟合后的带隙值为2.15 eV, 与图4中带边发射的发光峰接近. 图5(c)展示了基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器器件对不同波长光的响应特性曲线, 结果表明该器件对365~600 nm的入射光均有响应, 其中对365 nm波长的单色光具有最好的响应. 随后我们对该器件在365 nm波长入射光下的光电行为进行了系统的研究. 图5(d), (e)是分别在365 nm光照下, 不同光功率下的电流-电压和电流-时间响应特性曲线. 由图中可以看出, 基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器器件具有非常小的暗电流(25 fA), 随着光功率的增加, 器件的电流逐渐增大, 在不同强度的光照下均表现出良好的稳定性和较快的响应速度. 通过功率拟合公式

对光电流和入射光强度进行拟合^[33]:

$$I_{\text{ph}} \propto P^{\theta}, \quad (3)$$

其中, I_{ph} 代表光电流, P 是光功率密度, θ 是光功率依赖系数, 可以得出功率因子 $\theta=0.94$. 光电流和光强度呈现出接近线性的关系, 表明该器件的光电流产生机制主要为光电导效应(图S6). 为了量化基于 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的光探测器器件的光电性能, 我们对该器件的响应度($R_{\lambda}=I_{\text{ph}}/PS$, S 是有效面积), 探测度($D^*=R_{\lambda}S^{1/2}/(2eI_{\text{dark}})^{1/2}$, e 是电子电荷, I_{dark} 为器件的暗电流)和外量子效率($\text{EQE}=hcR_{\lambda}/e\lambda$, h 为普朗克常量, λ 为入射光的波长, c 为光速)进行了计算^[35,37]. 该器件在0.88 mW/cm²光照下, 响应度为110 mA/W, 探测度为 6.28×10^{11} Jones, 外量

子效率为37.5%。图5(g)是在89.46 mW/cm²光照下器件的光响应稳定性曲线, 得益于超低的暗电流, 该器件的开关比高达 4×10^4 。由于该器件的响应速度非常快, 通过增加激光频率配合超快模块对该器件的响应速度进行测试。图5(h), (e)是经过放大的一个循环内的电流-时间响应曲线, 定义光电流上升到最大值的90%所经历的时间为上升时间, 下降到最大值的10%的时间为下降时间^[36]。可以看出, 基于In_{2/3}PSe₃纳米片的光探测器件具有超快的光响应速度, 上升时间为14 μ s, 下降时间为24 μ s。透射电子显微镜表征和SHG强度面扫描成像等结果已经证明合成的In_{2/3}PSe₃晶体具有非常高的结晶性, 由于材料内部缺陷较少, 材料吸收光子产生的自由载流子不会被能级中的缺陷态捕获, 而是快速地生成电子-空穴对在偏压的作用下分离, 电子和空穴无阻碍地快速分离和复合是导致材料具有快速响应的主要原因^[38]。基于In_{2/3}PSe₃纳米片的光探测器件具有极低的暗电流、良好的探测度、高的开关比以及超快的响应速度, 表现出非常优异的光

电性能, 超过了大多数以前报道过的基于二维材料的紫外光探测器(表S1)^[14,39,40], 有望成为下一代光电子器件的有力竞争者。

3 结论

本研究采用化学气相输运法合成了高质量的In_{2/3}PSe₃单晶, 并通过机械剥离的方法获得了二维In_{2/3}PSe₃纳米片。借助二次谐波效应和光致发光光谱研究材料内部结构和缺陷对其非线性光学和发光性质的影响。二次谐波光谱结果证明In_{2/3}PSe₃具有本征对称性破缺的晶体结构; 光致发光光谱结果表明In_{2/3}PSe₃纳米片具有良好的发光特性和较长的荧光寿命。基于In_{2/3}PSe₃纳米片的光探测器件在紫外波段表现出良好的光响应特性, 在365 nm波长光照下, 光探测器件具有极低的暗电流(25 fA)、优异的探测度(6.28×10^{11} Jones)、高的开关比(4×10^4)以及超快的响应速度(14 μ s/24 μ s)。这些优异的光电性能表明In_{2/3}PSe₃纳米片在光电探测领域具有非常诱人的应用前景。

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补充材料

图S1 In_{2/3}PSe₃单晶的合成示意图和单晶的光学照片

图S2 二维In_{2/3}PSe₃纳米片的偏振拉曼光谱和In_{2/3}PSe₃拉曼峰强度随入射光角度变化的极化图

图S3 In_{2/3}PSe₃纳米片的元素能谱图

图S4 二维In_{2/3}PSe₃纳米片的SHG强度面扫描图

图S5 In_{2/3}PSe₃器件的光学显微镜照片

图S6 光电导效应的机理示意图

表S1 In₂P₃Se₉纳米片与其他二维材料的光电性能比较

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Summary for “二维 $\text{In}_{2/3}\text{PSe}_3$ 纳米片的制备及其光电探测性能”

Preparation and photodetection performance of two-dimensional $\text{In}_{2/3}\text{PSe}_3$ nanosheets

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Two-dimensional layered semiconductors have been the research focus of electronics and optoelectronics owing to their atomic thickness, light-matter interaction, and large-scale integration. Metal phosphorus trichalcogenides (MPTs), possessing the structure of $[\text{P}_2\text{S}_6]^{4-}$ or $[\text{P}_2\text{Se}_6]^{4-}$ surrounded with metal cations, have emerged as newly rising stars and drawn widespread interests of researchers due to their novel electrical and optical properties. Compared with common transition metal dichalcogenides, two-dimensional (2D) MPTs have larger optical bandgaps (from 1.3 to 3.5 eV), higher light absorption efficiency and richer bandgap structures due to the increased degree of freedom from the elements and atomic ratio, which highlight its great advantages in the field of optoelectronics. Among MPTs, $\text{In}_{2/3}\text{PSe}_3$ owns special structure, in which two-thirds of the octahedral holes are occupied by the indium ions and the other one-third are vacant. The unique structure endows $\text{In}_{2/3}\text{PSe}_3$ with intrinsic broken-symmetry, showing potential in non-linear optics. It was reported that bulk $\text{In}_{2/3}\text{PSe}_3$ is a direct-bandgap semiconductor (2.0 eV), in which the electron transition process from the conduction band to valence band is direct without phonon assisting, indicating great potential in application of optoelectronic devices. However, there is no research reported on the optoelectronic property of $\text{In}_{2/3}\text{PSe}_3$. According to the promising properties mentioned above, it is extremely urgent to characterize the optical and optoelectronic properties of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets. In this work, high-quality $\text{In}_{2/3}\text{PSe}_3$ single crystals are synthesized by chemical vapor transport method and for the first time we achieve 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets on SiO_2/Si substrate by mechanical exfoliation. X-ray diffractometer (XRD) and transmission electron microscope (TEM) are performed on $\text{In}_{2/3}\text{PSe}_3$ nanosheets, which demonstrate their high quality and single-crystalline nature. Considering that the non-centrosymmetric space group $R\bar{3}$, we further explored the SHG properties of $\text{In}_{2/3}\text{PSe}_3$ nanosheets. The intrinsic SHG response further verifies the broken-symmetry nature of $\text{In}_{2/3}\text{PSe}_3$. In addition, photoluminescence spectra of $\text{In}_{2/3}\text{PSe}_3$ nanosheets have revealed the exciton-like transition mechanism and longer PL lifetime than previously reported 2D materials, which may own to the high crystalline and low defects of as-synthesized crystals. To investigate the optoelectronic behavior of 2D $\text{In}_{2/3}\text{PSe}_3$ nanosheets, two-electrodes photodetectors based on $\text{In}_{2/3}\text{PSe}_3$ nanosheets are fabricated. Impressively, the $\text{In}_{2/3}\text{PSe}_3$ nanosheets-based photodetector exhibits an ultra-low dark current (25 fA), excellent detectivity (6.28×10^{11} Jones), high on/off ratio (4×10^4), and ultra-fast response rate (14 $\mu\text{s}/24 \mu\text{s}$) under 365 nm illumination, which are superior to other typical 2D ultraviolet photodetectors. The main photocurrent generation mechanism of the photodetector is photoconductive effect. The photogenerated free electrons and holes are separated rapidly to the opposite electrodes without trapping in defect states, leading to the ultra-fast response. These excellent optoelectronic behaviors of $\text{In}_{2/3}\text{PSe}_3$ nanosheet suggest its appealing prospect in future application of photodetection.

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