

基于功能基元序构策略提升 Ag_2Se 基柔性热电薄膜的性能

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摘 要: 热电材料是一种能够实现热能和电能相互转换的清洁能源材料。近年来, 随着可穿戴电子设备的蓬勃发展, 柔性热电材料成为研究热点。热电材料中载流子和声子传输表现出强耦合特性, 严重制约热电性能的提升。功能基元序构是一种优化材料性能的有效策略。在材料中构筑不同作用机制的功能基元, 并将功能基元进行序构, 同时增强功能基元间的协同效应, 可以有效地提升材料的性能。本工作主要以硒化银基柔性热电薄膜为例, 介绍功能基元序构和功能基元间协同效应对电、声输运性能和柔性的作用机制。

关键词: 热电薄膜; 硒化银; 功能基元序构; 柔性

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柔性热电器件由于具有稳定性高、无噪音、无污染、重量轻、体积小等优点, 在可穿戴电子设备的自供电和热管理等领域具有广泛的应用^[1-3]。热电器件的转换效率主要取决于热电材料的性能, 而热电材料的性能优劣由无量纲热电优值 zT 来衡量^[4]:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T, \text{ 式中: } \alpha \text{ 为 Seebeck 系数; } \sigma \text{ 为电导率; } \kappa \text{ 为热导率; } T \text{ 为绝对温度; } \alpha^2 \sigma \text{ 为功率因子(PF)。}$$

显然, 理想的热电材料应具有高 Seebeck 系数、高电导率和低热导率。然而, 材料的 α 、 σ 和 κ 3 个热电参数通过载流子浓度强烈耦合, 使获得高 zT 值面临诸多挑战^[5-6]。

柔性热电器件主要应用在室温附近, 因此需要研发出高性能的室温热电材料^[7-9]。 Bi_2Te_3 基材料是当前性能最好的室温热电材料^[10-12], 然而由于本征的脆性和刚性, 其不适合直接用于制作柔性热电器件。相对于无机材料, 导电聚合物具有质量轻、热导率低和柔性好等特点, 但其 zT 值较低。目前, 常见的导电聚合物有聚 3,4-乙撑二氧噻吩(PEDOT)^[13]、聚苯胺(PANI)^[14]、聚吡咯(PPy)^[15]和聚 3-己基噻吩(P3HT)^[16]等。为此, 研究人员将导电聚合物与无机热电材料复合, 形成导电聚合物/无机热电复合材

料, 希望利用导电聚合物的热导率低及柔性好和无机热电材料的功率因子高的优点。Wang 等^[17]先以模板法制备出粒径不同且均匀的 Bi_2Te_3 纳米颗粒阵列, 再用气相聚合法在 Bi_2Te_3 纳米颗粒阵列之间原位聚合 PEDOT, 最终获得两相复合的薄膜材料, 室温功率因子可达 $1\,350\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。近年, 研究人员将无机热电材料沉积在柔性衬底上, 制备出柔性较为理想的高性能热电薄膜。如 Tony 等^[18]采用丝网印刷工艺将 $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3/\text{Te}$ 无机相沉积在聚酰亚胺膜(PI)衬底上, 经过热压烧结, 制备出的柔性复合热电薄膜的室温功率因子高达 $3\,000\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。此外, Jin 等^[19]利用磁控溅射技术在单壁碳纳米管(SWCNT)支架上沉积层状结构的 Bi_2Te_3 , 制备出的 $\text{Bi}_2\text{Te}_3/\text{SWCNT}$ 自支撑复合热电薄膜的室温功率因子和 zT 分别达到 $1\,600\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 和 0.89。 Bi_2Te_3 中 Te 的地壳丰度低、毒性高等因素, 故其不适合用于可穿戴电子设备供电的柔性热电器件。

Ag_2Se 因具有较高的室温热电性能、相对高的元素地壳丰度和环境友好的化学组分等优点, 有望取代传统的 Bi_2Te_3 基室温热电材料^[20-25]。Ferhat 等^[20]报道了 Ag_2Se 块体材料的室温功率因子高达 $3\,500\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。Hou 等^[22]采用热蒸发法在柔性 PI

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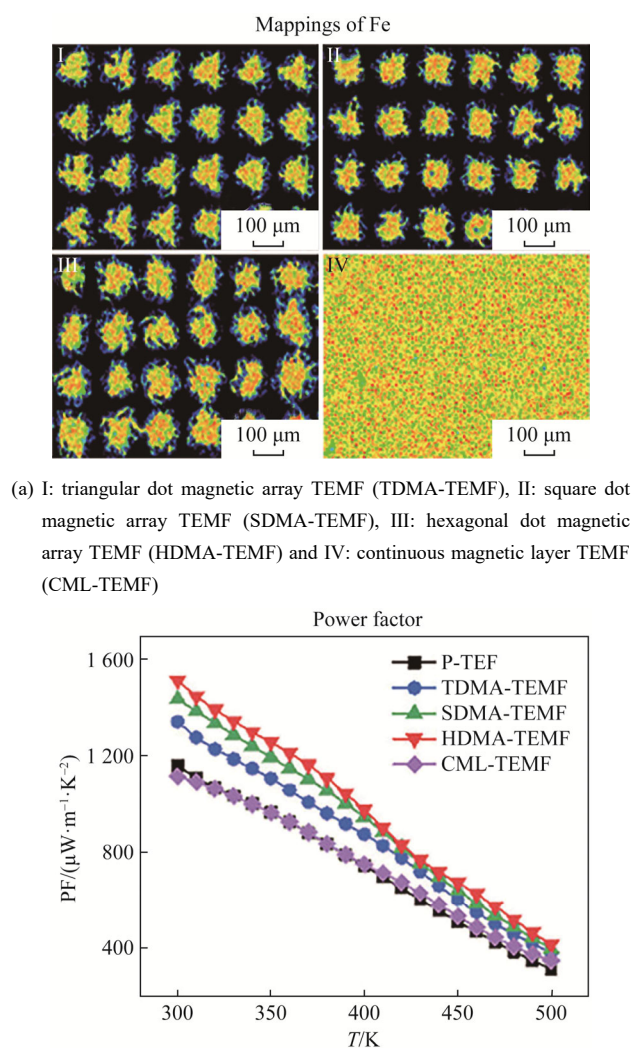
衬底上生长沿 c 轴取向的 $\text{Ag}_{1.8}\text{Se}$ 薄膜, 室温功率因子达到 $1700 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。Lei 等^[23]通过在 PI 衬底上溅射 Ag 膜, 然后将其浸入 $\text{Se}/\text{Na}_2\text{S}$ 混合溶液, 进行硒化反应 1 min, 制备出由面内方向随机取向和面外方向[201]择优取向的柱状晶组成的 Ag_2Se 薄膜, 在 300 K 的功率因子和 zT 值分别达到 $2590 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 和 1.2。然而, 该工艺制备的 Ag_2Se 薄膜的厚度非常薄(小于 $2 \mu\text{m}$), 因此, 由其制备的器件内阻将会很大, 会阻碍其实际应用。

本课题组开发了一种利用湿化学合成的 Ag_2Se 纳米线, 结合真空抽滤和热压的方法制备基于尼龙滤膜的 Ag_2Se 柔性薄膜, 并取得一系列进展^[26-35]。如 Jiang 等^[29]将 Ag_2Se 纳米线的合成温度从室温提升至 40°C , 通过真空抽滤和热压处理, 获得致密度较高的 Ag_2Se 薄膜, 在 300 K 的功率因子达 $1882 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。

研究人员采用多种策略如优化载流子浓度^[36]、能带工程^[37]和纳米结构工程^[38]等来提高无机热电材料的 zT 值, 并取得了显著的进展。2020 年, 国家自然科学基金委员会实施了功能基元序构的高性能材料基础研究重大项目, 国内很多研究人员开始重视基于功能基元的材料设计方法。如 Zhang 等^[39]基于功能基元的材料设计方法, 发现线性三原子共振键(LTRB)在结构上具有强的各向异性及强的非谐声子散射, 且含 LTRB 的化合物的晶格热导率都较低。引入 LTRB 作为功能基元, 筛选潜在的热电材料。以 K_5CuSb_2 为例具体分析了基元 $[\text{Sb}-\text{Cu}-\text{Sb}]^{5-}$ 的共振电子结构, 阐释了 LTRB 功能基元与热电性能之间的关系。Tang 等^[40]在 SnSe 中引入 PbSe 量子点功能基元, 显著提升了 SnSe 基热电材料的性能。结果表明, PbSe 量子点功能基元使材料的态密度显著提升, 进而提升了 Seebeck 系数和功率因子。 PbSe 量子点功能基元和晶格应变有效地散射声子, 显著降低晶格热导率, 全温段范围的平均 zT 值达到 0.71。

最近, “功能基元序构的高性能材料”的研究新范式受到了广泛的关注, 通过对功能基元的研究和有序组装可获得高性能材料^[41-46]。研究人员发现 AgSbTe_2 体系中原子尺度有序能改变 Fermi 能级位置, 提高材料的电导率; 同时产生的微区应变波纹可以降低热导率, 从而提高材料的热电性能^[47]。在热电材料中嵌入磁功能基元是提高热电性能的有效方法^[48-50]。为了研究磁功能基元的有序排列对热电性能的影响, 如图 1 所示, Zhao 等^[51]采用 2 步丝网印刷工艺结合热压工艺, 制备出具有点磁阵列的

$\text{Fe}/\text{Bi}_{0.5}\text{Sb}_{0.5}\text{Te}_3$ /环氧树脂柔性热电磁薄膜。结果表明, Fe 磁功能基元的序构使薄膜磁层具有较高的矫顽力, 载流子浓度增加的同时获得较高的载流子迁移率。因此, 在保持较高 Seebeck 系数的同时, 电导率显著提高。六边形点磁阵列热电磁薄膜在 300 K 的功率因子达到了 $1510 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$, 与原始热电薄膜和连续磁层热电磁薄膜相比分别提高了 33.6% 和 36.1%。因此, 如果 Ag_2Se 热电薄膜中实现功能基元序构, 其性能有望进一步提升。下面以对 Ag_2Se 基热电薄膜的研究为例, 介绍功能基元序构和功能基元间协同效应对提升热电性能和柔性的影响机制。



PF is power factor.

(b) Power factor versus temperature of the P-TEF and four TEMFs

图 1 4 种热电磁薄膜(TEMF)的 Fe 元素的 Mapping 图和原始热电薄膜(P-TEF)及 4 种热电磁薄膜的功率因子随温度的变化图^[51]

Fig. 1 Mappings of Fe element of the four thermoelectromagnetic films (TEMFs) and Power factor versus temperature of the pristine TE film (P-TEF) and four TEMFs^[51]

1 功能基元序构的 Ag_2Se 基柔性热电薄膜

1.1 通过 Ag 与 Se 和 Ag 与 S 亲和性不同实现功能基元序构的 Ag–S–Se 三元复合薄膜

与 Se 相比, S 元素的地壳含量丰富, 成本较低, 同时 S 的毒性也较小。此外, Ag_2S 具有良好的本征塑性^[52]。Wu 等^[53]采用湿化学法在室温合成 Se 纳米线和在 120 °C 合成 Ag_2S 亚微米颗粒; 随后按照 Se 纳米线与 Ag_2S 的摩尔比值为 0.7:1.0, 在 90 °C 进行湿化学反应, 制备出 Ag–Se–S 三元合金粉末; 然后真空抽滤沉积于尼龙滤膜上, 在 230 °C/MPa 的条件下热压 30 min, 最终制备出以 S 掺杂 Ag_2Se 为“核”和 Se 掺杂 Ag_2S 和非晶态 S 混合相为“壳” (厚度约 15 nm) 的微纳结构构筑的复合薄膜, 其在 300 K 的功率因子达到 $954 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ (图 2)。

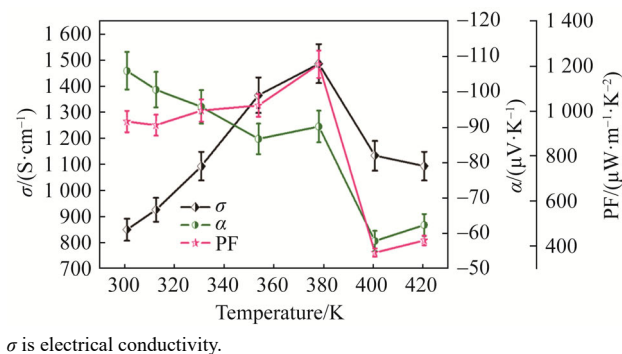
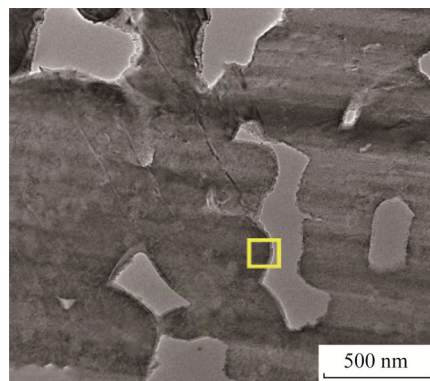


图 2 S 掺杂 Ag_2Se 薄膜的变温热电性能^[53]

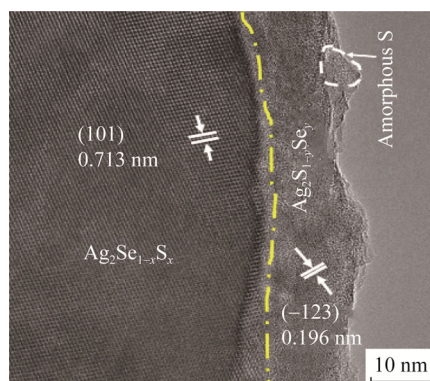
Fig. 2 Temperature dependence of thermoelectric properties of S-doped Ag_2Se film^[53]

图 3 为 S 掺杂 Ag_2Se 薄膜的内部显微结构。由图 3a 可见, 薄膜具有多孔的类网络状结构, 样品本身在图 3a 中呈现暗黑色, 孔洞在图 3a 中呈现浅灰色。图 3b 为图 3a 中黄色方框的局部放大图。由图 3b 可见, 整个晶粒由内“核” (S 掺杂 Ag_2Se , 晶粒结晶良好) 和外“壳” (Se 掺杂 Ag_2S 和非晶态 S) 组成。从图 3c 可以更加清楚地看到“核”与“壳”2 部分的相界面。图 3d 为 1 个三角气孔区域的 S、Se、Ag 元素的面扫描图, 发现在三角形气孔的边缘有非常明显的 S 元素富集, 而 Se 元素和 Ag 元素相对较少。此外, 这种“核–壳”结构是普遍存在的。

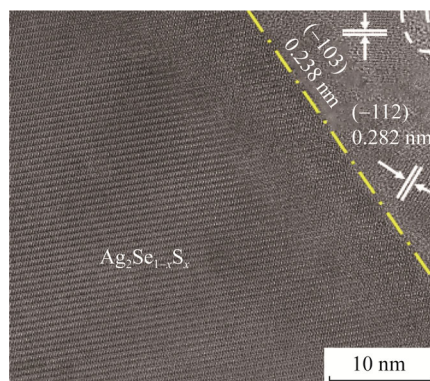
“核–壳”结构中“核”结晶良好, 构成导电通道, 确保薄膜具有好的电性能, 即热电功能基元。而“壳”中的 Ag_2S 具有良好的本征塑性, 非晶态 S 也有很好的塑性, 即“壳”相当于柔性功能基元, 确保薄膜具有极好的柔性 (绕半径为 4 mm 棒弯曲测试 2 000 次



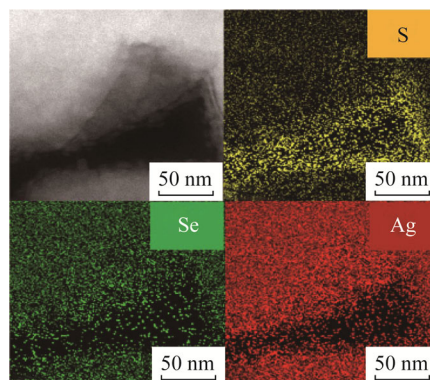
(a) Typical transmission electron microscopy (TEM) image



(b) Enlarged image of the yellow square marked in (a)



(c) Enlarged images of two-phase interface of yellow square marked in (a)



(d) HAADF-STEM image and the corresponding elemental mapping of S, Se, and Ag

图 3 S 掺杂 Ag_2Se 薄膜的内部显微结构^[53]

Fig. 3 Internal microstructure of S-doped Ag_2Se film^[53]

后, 薄膜的电导率仍保持原来的 94.4%), 柔性明显优于 Ag_2Se 薄膜(绕半径为 4 mm 棒弯曲测试 1000 次后, 薄膜的电导率保持原来的 93%)^[26]。

这种“核-壳”结构的形成主要是由于 Ag 与 Se 和 Ag 与 S 的亲性不同。在热压过程中, 尺寸(小于 100 nm)小的 S 掺杂 Ag_2Se 颗粒由于纳米效应会率先熔化, 熔融的 S 掺杂 Ag_2Se 接触到未熔融的大颗粒时, 会促进后者的熔融; 随着热压的进行, 越来越多的 S 掺杂 Ag_2Se 熔化并形成 Ag-Se-S 的三元黏流体。从溶度积数值 $K_{\text{sp}}(\text{Ag}_2\text{Se})=2.0\times 10^{-64}$ 、 $K_{\text{sp}}(\text{Ag}_2\text{S})=6.3\times 10^{-50}$ 可知^[54], Se 和 Ag 的亲性要高于 S 和 Ag 的亲性, Ag_2Se 会率先从熔体中析出, 随后形核结晶长大, 再在它的表面形成 Ag_2S 和非晶 S。由于 Ag、Se 和 S 处于黏流态, 流动性受限, 当 Ag_2Se 率先形核时, 不可避免会掺入少量 S; 同样地, 在形成外壳时, 也会有少量 Se 掺杂进 Ag_2S , 加上热压的作用, 最终形成 S 掺杂 Ag_2Se 为“核”和 Se 掺杂

Ag_2S 和非晶态 S 混合相为“壳”的微纳结构组成的复合薄膜。

此外, 因为薄膜主要由 S 掺杂 Ag_2Se 与少量 Se 掺杂 Ag_2S 和非晶 S 单质组成, 而 3 者的热导率都很低(300 K 时, Ag_2Se ^[55]和 Ag_2S ^[56]的热导率分别为 $0.65 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 和 $0.60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, 非晶态 S 的热导率更低); 并且薄膜含有大量不同尺度的显微结构(图 4), 比如多种类型的界面、纳米到亚微米尺度的孔洞、层错、晶界等, 因此, 该薄膜具有较低的热导率。

在该体系中通过构筑“核-壳”结构的功能基元序构, 强化了功能基元间的协同效应, 从而同时获得高热电性能和高柔性。值得一提的是, 在该体系中, 控制 Se 纳米线与 Ag_2S 的摩尔比至关重要。当 Se 纳米线与 Ag_2S 的摩尔比值 ≤ 0.6 时, 薄膜中没有出现“核-壳”结构, 而是均匀的 Se 掺杂 Ag_2S 相^[57]。

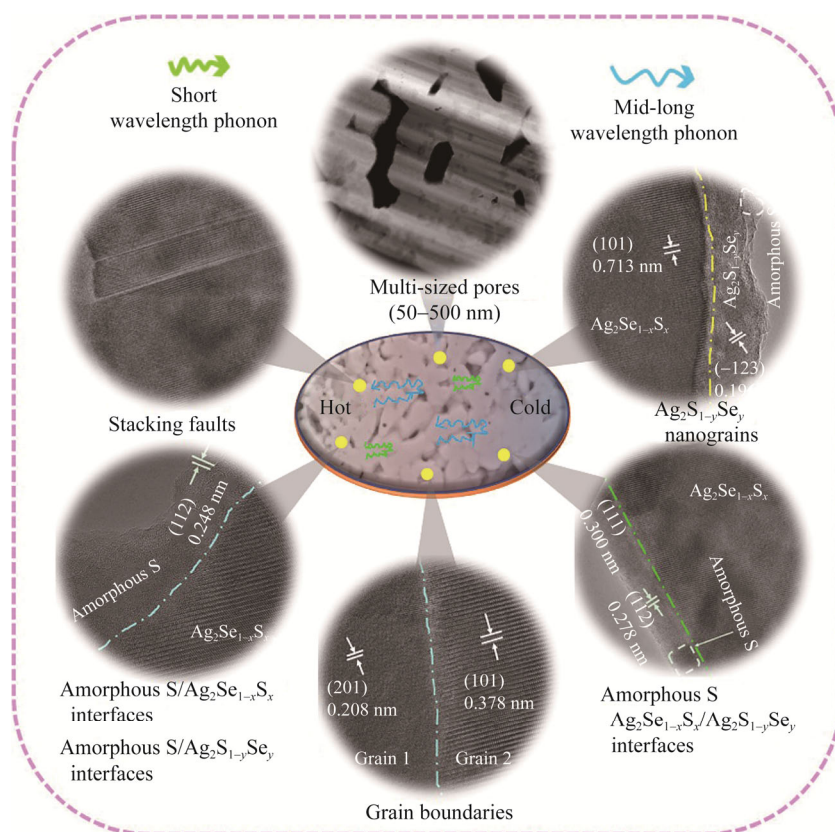


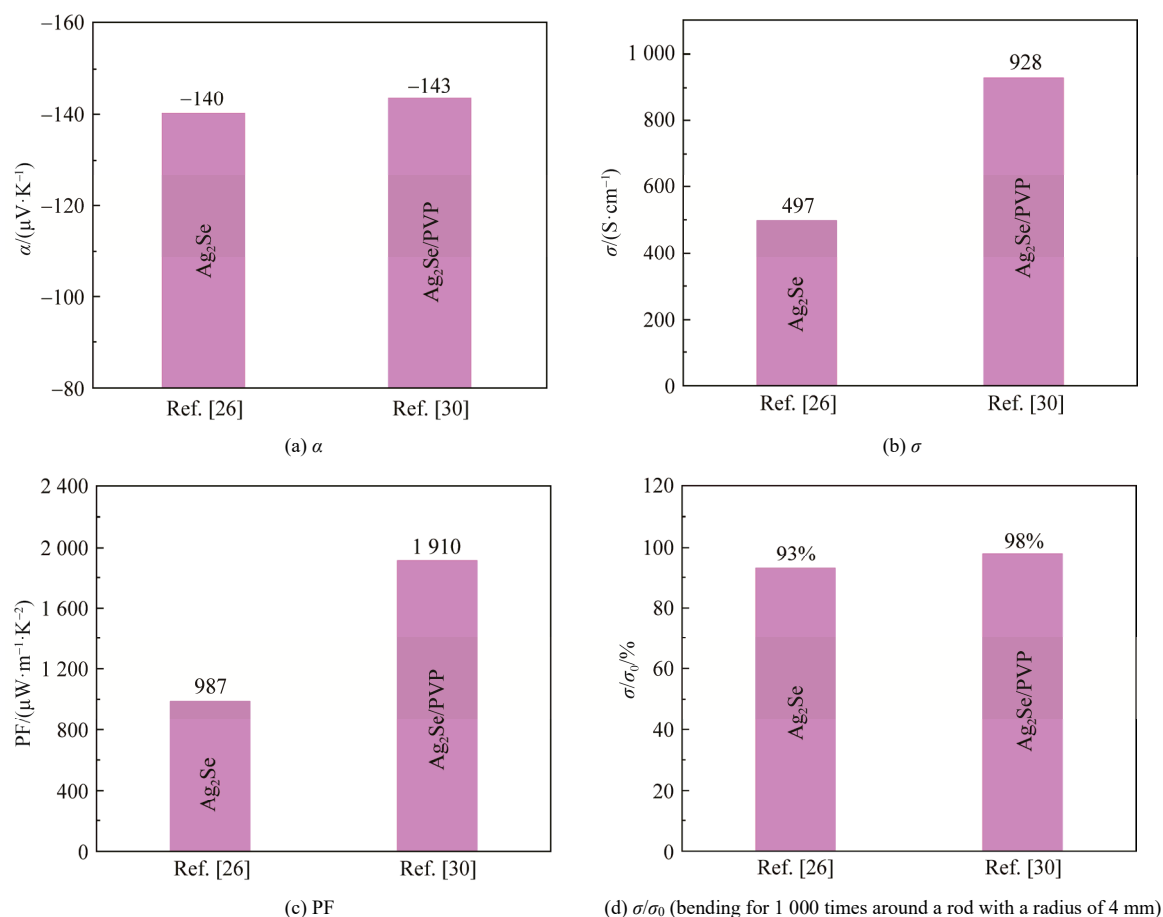
图 4 S 掺杂 Ag_2Se 薄膜的声子散射机制示意图^[53]

Fig. 4 Schematic illustration of phonon scattering mechanisms in the S-doped Ag_2Se film^[53]

1.2 绝缘聚合物聚乙烯吡咯烷酮(PVP)与 Ag_2Se 复合

PVP 是一种绝缘聚合物, 具有附着力好、毒性低、价格低等特点, 并且在极性和非极性溶剂中溶解度高^[58]。Jiang 等^[30]以 Se 纳米线为模板, 在 40 °C

合成 PVP (厚度: 5~10 nm)原位包覆的 Ag_2Se 纳米结构; 然后通过真空抽滤将其沉积在尼龙滤膜上, 在 200 °C/MPa 热压 30 min, 制备出的 Ag_2Se /PVP 复合薄膜具有很高的功率因子和优异的柔性。图 5



α is seebeck coefficient.

图5 Ag₂Se 薄膜^[26]与 Ag₂Se/PVP 复合薄膜^[30]在 300 K 的热电性能和柔性对比

Fig. 5 Comparison of thermoelectric properties and flexibility at 300 K of Ag₂Se film^[26] and Ag₂Se/PVP composite film^[30]

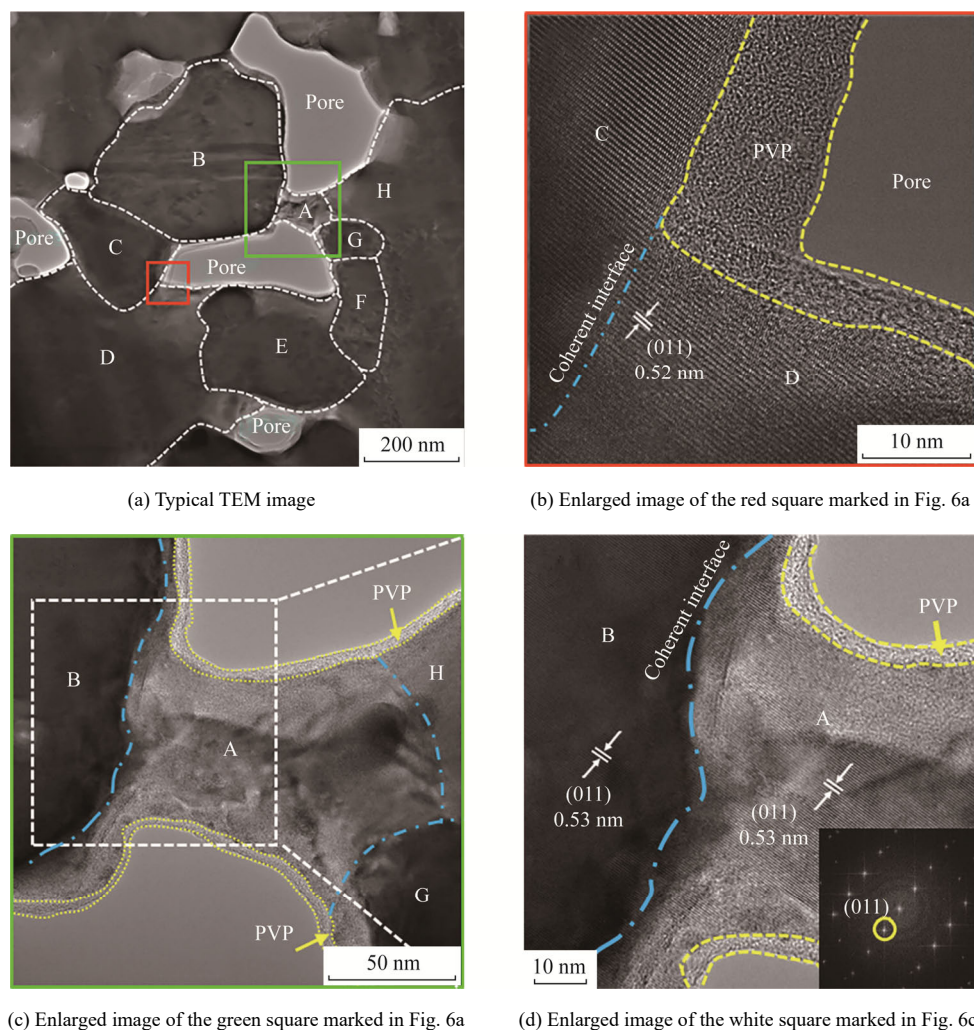
为 Ag₂Se 薄膜^[26]与 Ag₂Se/PVP 复合薄膜^[30]在 300 K 的热电性能和柔性对比图。由图 5a~图 5c 可见, 与 Ag₂Se 薄膜相比, Ag₂Se/PVP 复合薄膜的 Seebeck 系数($-143 \mu\text{V}\cdot\text{K}^{-1}$)略有提升, 电导率从 $497 \text{ S}\cdot\text{cm}^{-1}$ 增加到 $928 \text{ S}\cdot\text{cm}^{-1}$, 功率因子从 $987 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 增加到 $1910 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。由图 5d 可见, Ag₂Se/PVP 复合薄膜绕半径为 4 mm 棒弯曲 1000 次后, 电导率仍保持 98%, 柔性好于 Ag₂Se 薄膜^[26], 这主要是因为 PVP 的粘合作用。

图 6 为 Ag₂Se/PVP 复合薄膜的内部显微结构。由图 6a 可见, 薄膜具有多孔结构, 图中孔隙呈灰色, Ag₂Se 晶粒呈暗黑色。由图 6b 和图 6c 可见, PVP (厚度: 5~10 nm) 存在于在纳米孔壁处。薄膜中的 PVP 包裹的纳米孔洞, 能够散射声子、降低热导率, 从而提高 zT 值。此外, 薄膜中还存在晶粒共格(图 6b 和图 6d), 因此认为相邻 Ag₂Se 晶粒共格是复合薄膜具有高电导率的主要原因。

添加 PVP 后, Ag₂Se 晶粒共格, 这与 Ag₂Se/PVP 纳米结构的烧结机理有关, 其烧结过程推测如下:

在热压过程中, 由于 Ag₂Se 纳米结构表面包覆了 1 层 PVP 纳米层, 当温度低于 PVP 熔点(130°C)时, 不会发生烧结。当温度高于 130°C 时, PVP 熔化。由于受压, 刚性 Ag₂Se 纳米结构与邻近的 Ag₂Se 纳米结构接触, 并将接触部位熔融的 PVP 挤压到附近的孔隙中, 形成以 PVP 包裹的纳米孔洞。由于熔融的 PVP 黏性较大, 接触部位之外的 PVP 仍然会粘附在纳米结构的表面。烧结从接触部位开始, 由于接触面积小, 热压条件($200^\circ\text{C}\times 1 \text{ MPa}$)又非常温和, 烧结进程缓慢, 加上 PVP 的导向作用^[59], 相邻的 Ag₂Se 晶粒倾向于共格, 实现 Ag₂Se 热电功能基元序构。

此外, 由于 PVP 本征的低热导率、Ag₂Se/PVP 异质界面和纳米孔洞能够有效地散射声子, 虽然复合薄膜的电导率有大幅提升, 其热导率($0.508 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)略高于 Ag₂Se 薄膜的热导率($0.478 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)^[26]。在该体系中构筑 PVP 功能基元和 Ag₂Se 热电功能基元序构, 并且得益于这 2 种功能基元的协同作用, 实现了对复合薄膜中电子/声子运输的有效调控, 显著提高了热电性能和柔性。

图 6 $\text{Ag}_2\text{Se}/\text{PVP}$ 复合薄膜的内部显微结构^[30]Fig. 6 Internal microstructure of $\text{Ag}_2\text{Se}/\text{PVP}$ composite film^[30]

1.3 导电聚合物聚吡咯(PPy)与 Ag_2Se 复合

与 PEDOT、PANI 等相比, PPy 的价格相对便宜。Li 等^[35]以 Se 纳米线为模板, 在 40°C 合成 Ag_2Se 纳米结构; 然后通过原位聚合方法在 Ag_2Se 纳米结构上包覆 1 层几纳米厚的 PPy; 将 PPy 包覆的 Ag_2Se 纳米结构通过真空抽滤沉积在尼龙膜上, 在 $230^\circ\text{C}/\text{MPa}$ 条件下热压 30 min, 获得具有极高功率因子和优异柔性的 $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜。图 7 为 Ag_2Se 薄膜^[29]与 $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜^[35]在 300 K 的热电性能和柔性对比图。由图 7a~图 7c 可见, 与 Ag_2Se 薄膜相比, $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜的 Seebeck 系数保持在 $-144\ \mu\text{V}\cdot\text{K}^{-1}$, 电导率从 $920\ \text{S}\cdot\text{cm}^{-1}$ 提升至 $1064\ \text{S}\cdot\text{cm}^{-1}$, 功率因子从 $1882\ \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 提升至 $2240\ \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ 。由图 7d 可见, 由于 PPy 的良好黏性与附着力, 复合薄膜绕半径为 4 mm 棒弯曲 1500 次后, 仍保留 92.5% 的电导率, 柔性优于 Ag_2Se 薄膜^[29]。

图 8 为 $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜的内部显微结构。图 8a 为典型的高角环形暗场(HAADF)-扫描透射电镜(STEM)照片, 显示了 1 晶界。图 8b 为图 8a 中紫色方框的局部放大图。由图 8b 可见, 晶界没有缺陷且连续。图 8c 为结晶性优异的晶粒的高分辨扫描透射电镜(HRSTEM)照片。由图 8c 可见, Ag_2Se 晶粒具有优异的结晶性。 $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜内的 Ag_2Se 晶粒优异的结晶性、晶界没有缺陷且连续, 表明成功构筑 Ag_2Se 热电功能基元序构, 这是复合薄膜保持高电导率的主要原因之一。

添加 PPy 后, Ag_2Se 晶粒结晶性良好且晶界连续, 这与 $\text{Ag}_2\text{Se}/\text{PPy}$ 纳米结构的烧结机理有关, 其烧结过程推测如下: 在热压过程中, Ag_2Se 纳米结构熔化, 但 PPy 只是软化(其熔点大于 300°C ^[60]), 软化的 PPy 包裹熔融的 Ag_2Se 并形成“微胶囊”结构。随着温度升高及压力的作用, 微胶囊局部破裂, 使相邻的微胶囊中的 Ag_2Se 熔体汇聚形成较大的微胶

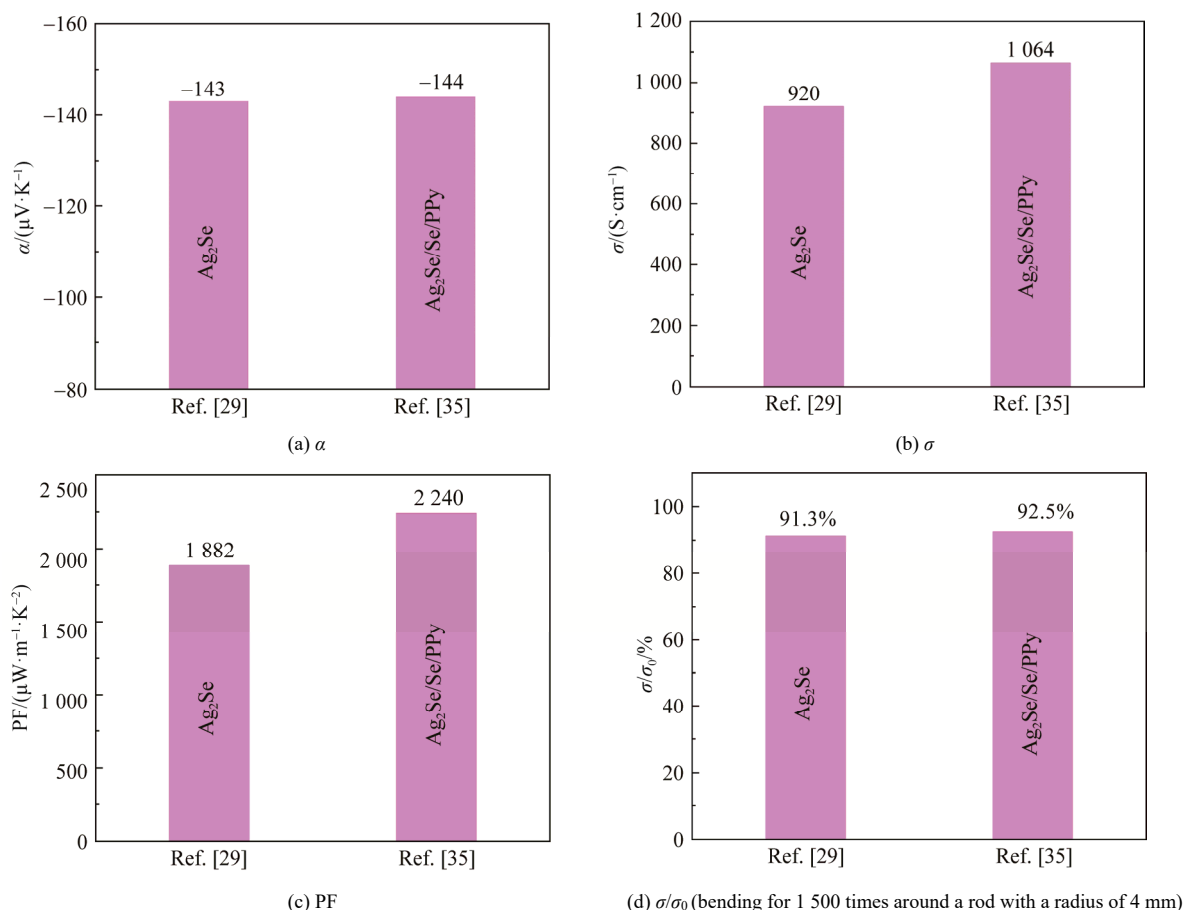


图7 Ag_2Se 薄膜^[29]与 $\text{Ag}_2\text{Se/Se/PPy}$ 复合薄膜^[35]在 300 K 的热电性能和柔性对比图

Fig. 7 Comparison of thermoelectric properties and flexibility at 300 K of Ag_2Se film^[29] and $\text{Ag}_2\text{Se/Se/PPy}$ composite film^[35]

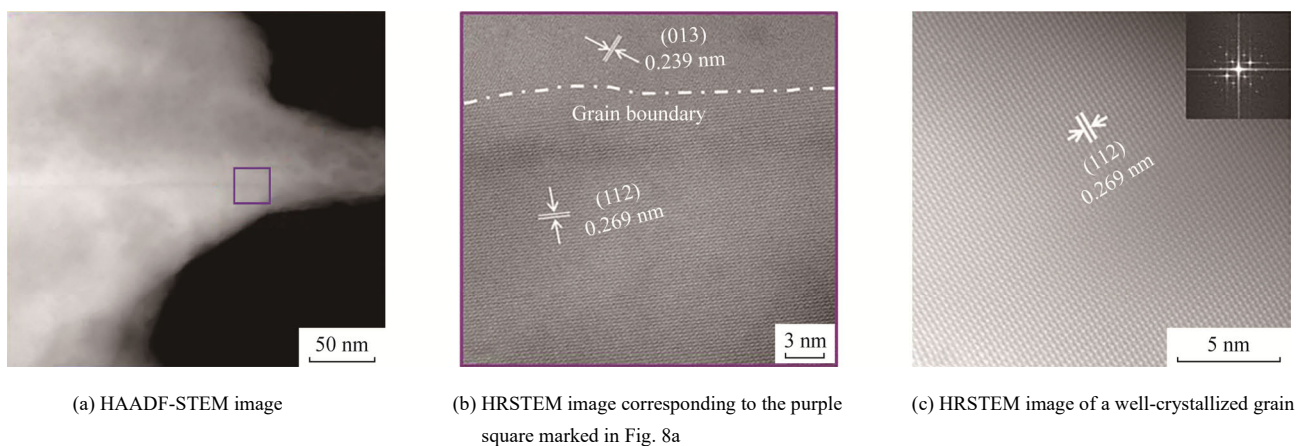


图8 $\text{Ag}_2\text{Se/Se/PPy}$ 复合薄膜的内部显微结构^[35]

Fig. 8 Internal microstructure of the $\text{Ag}_2\text{Se/Se/PPy}$ composite film^[35]

囊, 然后形核结晶。为了降低表面能: 大晶粒生长而小晶粒逐渐消失, 形成亚微米到微米的 Ag_2Se 等轴晶, 而 PPy 位于晶粒的表面, 并且 Ag_2Se 晶粒中含有少量 Se 纳米晶夹杂物。此外, 由于 PPy 的包覆, Ag_2Se 的烧结仅发生在 210~230 °C 之间。

图9为 $\text{Ag}_2\text{Se/Se/PPy}$ 复合薄膜的能量过滤效应

机制。图9为 Ag_2Se 和 PPy 的完整能带图。由图9a可见, Ag_2Se 薄膜的功函数(Φ)值、能带带隙(E_g)和电子亲和力(χ)分别为 5.58、1.5 eV 和 4.99 eV, 而 PPy 的功函数值、能带带隙和电子亲和力分别为 4.58、2.85 eV 和 3.05 eV。平衡 2 组分 Fermi 能级(E_F)后的能带图如图 9b 所示。由图 9b 可见, Ag_2Se 与 PPy

的界面势垒(Φ_b)为 1.00 eV, 因此 $\text{Ag}_2\text{Se}/\text{PPy}$ 界面具有能量过滤效应, 即低能载流子被 $\text{Ag}_2\text{Se}/\text{PPy}$ 界面阻挡, 高能载流子可以通过。此外, 复合薄膜中存在少量的 Se 纳米晶(20 nm), 几乎不会对电导率造成影响。同时, 在 $\text{Ag}_2\text{Se}/\text{Se}$ 异质界面处会产生能量过滤效应, 如图 9c 所示。复合薄膜中 $\text{Ag}_2\text{Se}/\text{PPy}$ 和 $\text{Ag}_2\text{Se}/\text{Se}$ 异质界面产生的能量过滤效应, 使复合薄膜具有高电导率的同时, 还能保持较高的 Seebeck 系数。由于 PPy 的本征低热导率、复合薄膜中纳米到亚微米的孔洞、Se 纳米晶夹杂物、 $\text{Ag}_2\text{Se}/\text{PPy}$ 和

$\text{Ag}_2\text{Se}/\text{Se}$ 异质界面能够有效地散射声子, 复合薄膜的热导率($0.714 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)仅略高于 Ag_2Se 薄膜的热导率($0.706 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)^[29]。在该体系中构筑 PPy 功能基元和 Ag_2Se 热电功能基元序构, 且得益于这 2 种功能基元的协同作用, 复合薄膜具有很高的热电性能和优异的柔性。

表 1 对比了 Ag_2Se 薄膜与功能基元序构的 Ag_2Se 基薄膜在 300 K 的热电性能和柔性。由表 1 可知, 在 Ag_2Se 薄膜中构筑不同功能基元序构, 能够提升热电性能和柔性。

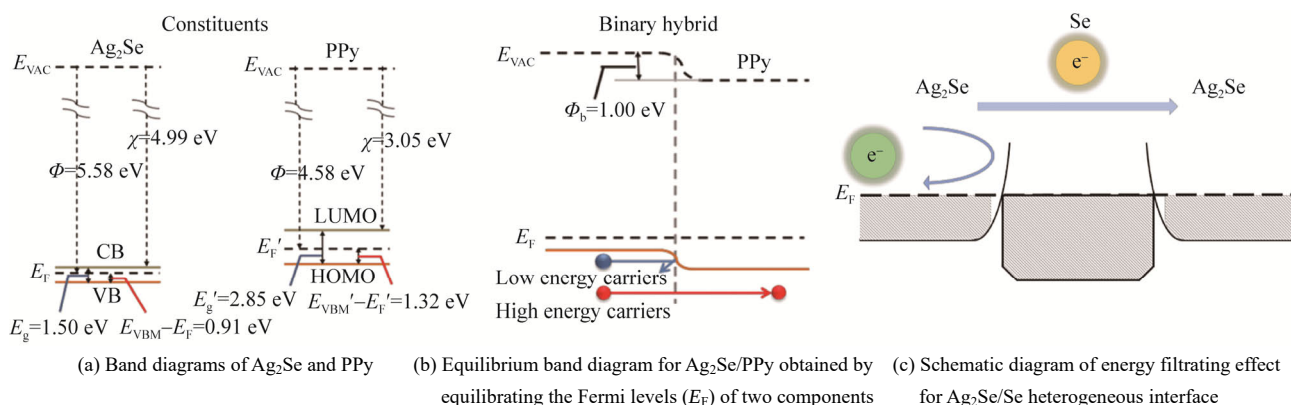


图 9 $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ 复合薄膜的能量过滤效应机制^[35]

Fig. 9 Energy-filtering effect mechanism of $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ composite film^[35]

表 1 Ag_2Se 薄膜与功能基元序构的 Ag_2Se 基薄膜在 300 K 的热电性能和柔性对比

Table 1 Comparison of thermoelectric properties and flexibility at 300 K of Ag_2Se film and Ag_2Se -based film with functional units ordering

Sample	Functional units ordering (Yes or No)	$\alpha/(\mu\text{V}\cdot\text{K}^{-1})$	$\sigma/(\text{S}\cdot\text{cm}^{-1})$	$\text{PF}/(\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2})$	Flexibility (bending radius~4 mm, σ/σ_0)	Reference
S doped Ag_2Se	Yes (Core-Shell)	-106	849	954	94.4% (2 000 times)	[53]
Ag_2Se	No	-140	497	987	93.0% (1 000 times)	[26]
$\text{Ag}_2\text{Se}/\text{PVP}$	Yes (Coherent grain)	-143	928	1 910	98.0% (1 000 times)	[30]
Ag_2Se	No	-143	920	1 882	91.3% (1 500 times)	[29]
$\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$	Yes (Continuous grain boundary)	-144	1 064	2 240	92.5% (1 500 times)	[35]

2 结论与展望

无机热电半导体通常具有较高的 zT 值, 但其柔性化过程往往对其性能有负面影响。如何制备既保持无机热电半导体的热电转化能力又能大幅度提高其柔性的热电薄膜将是未来重要的研究方向。功能基元序构策略是优化材料性能的有效手段。本文以 Ag_2Se 基热电薄膜为例, 通过构筑相邻 Ag_2Se 晶粒共格、完好的结晶及连续的晶界和“核-壳”结构等热电功能基元序构和柔性功能基元序构, 结合不同作用的功能基元间的协同效应, 实现了对电子、声子传输和柔性的有效调控, 使得薄膜的电导率提升、

热导率降低和柔性提升。相关的措施是否具有普适性尚需更多实验的验证。

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Enhanced Performance of Ag_2Se -Based Flexible Thermoelectric Films Based on Functional Units Ordering Strategy

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Extended Abstract

Thermoelectric (TE) materials as one of clean energy materials can realize the direct conversion between heat and electricity. Flexible TE films have attracted recent attention because they can be used to fabricate flexible TE generators (f-TEGs) to replace batteries that need to be charged or replaced frequently to power rapidly developing wearable electronic devices. Bi_2Te_3 -based films exhibit the optimum TE performance at room temperature (RT), but Bi_2Te_3 -based films are easy to oxidize, and Te is expensive, rare, and toxic, so suitable alternatives need to be explored. Silver selenide (Ag_2Se) is a narrow bandgap semiconductor and has a superior TE performance at RT. Furthermore, compared with element Te, element Se is less toxic and more abundant. However, the TE properties of Ag_2Se are still lower than that of Bi_2Te_3 . This review summarized the mechanism of improving the TE properties and flexibility of Ag_2Se by functional unit order strategy, and provided a route to enhance the TE properties and flexibility of Ag_2Se .

Typical strategies for improving the zT values of Ag_2Se -based films include the introduction of secondary phase, defect engineering, stoichiometry manipulation, etc.. However, charge carrier and phonon transport in TE material are strongly coupled with each other, seriously restricting the improvement of TE performance. The functional unit order is an effective strategy to optimize the performance of materials. Functional units with different roles constructed orderly in materials can enhance a synergistic effect between functional units and thus improve the performance. For Ag_2Se -based flexible TE films, the effect of functional unit ordering and the synergetic effect between functional units on the electronic, phonon transport, and flexibility were discussed. The S-doped Ag_2Se film shows a power factor $\sim 954 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ at 300 K and superior flexibility (94.4% of the original electrical conductivity

was preserved after bending for 2 000 times around a rod with a radius of 4 mm). The S-doped Ag_2Se film consists of a special “core–shell” microstructure, namely, the “core” is an S-doped Ag_2Se phase and the “shell” (thickness of 15 nm) is Se-doped Ag_2S and amorphous S mixed phase. The formation of the “core–shell” microstructure is mainly due to the different affinities between Ag and Se and Ag and S. The “core” acts as TE functional units because of the well-preserved conductive paths formed by well-crystallized S-doped Ag_2Se grains, thus maintaining a high electrical conductivity of the film. The “shell” acts as a flexible functional unit to enhance the flexibility of the film mainly due to the inherently flexible amorphous S phase and the ductile Se-doped Ag_2S . Moreover, the thermal conductivity of the film is low because of the strengthened phonon scattering resulting from the hetero-interfaces and the intrinsically low thermal conductivity of the amorphous S phase and the Se-doped Ag_2S nanograins.

The $\text{Ag}_2\text{Se}/\text{PVP}$ composite film has a high power factor of $\sim 1\,910\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and a superior flexibility at 300 K. Most Ag_2Se grains with coherent interfaces in the $\text{Ag}_2\text{Se}/\text{PVP}$ composite film indicate that the Ag_2Se TE functional unit is constructed, leading to a high electrical conductivity. The formation of the unique microstructure is related to the special sintering mechanism and the effect of PVP. The superior flexibility (*i.e.*, 98% of the original electrical conductivity is preserved after bending for 1 000 times around a rod with a radius of 4 mm) is due to the good adhesion and viscosity of PVP acting as a flexible functional unit. The composite film has a pretty low thermal conductivity because of PVP with an extremely low intrinsic thermal conductivity and it contains numerous nano-sized- to micron-sized-pores and $\text{Ag}_2\text{Se}/\text{PVP}$ hetero-interfaces.

The $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ composite film has an exceptionally high power factor of $\sim 2\,240\,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and excellent flexibility at 300 K. The $\text{Ag}_2\text{Se}/\text{Se}/\text{PPy}$ composite film has a superior crystallinity of Ag_2Se grains and continuous grain boundaries without defects, indicating that the Ag_2Se TE functional unit is constructed, leading to a high electrical conductivity. There exist energy-filtering effects at the heterointerfaces of $\text{Ag}_2\text{Se}/\text{Se}$ and $\text{Ag}_2\text{Se}/\text{PPy}$ in the film, leading to a high Seebeck coefficient. The formation of the unique microstructure is related to the special sintering mechanism. The superior flexibility (*i.e.*, 92.5% of the original electrical conductivity is preserved after bending for 1 500 times around a rod with a radius of 4 mm) is due to the good adhesion and viscosity of PPy acting as a flexible functional unit. Moreover, the nano-sized to submicron-sized pores, and the $\text{Ag}_2\text{Se}/\text{PPy}$ and $\text{Ag}_2\text{Se}/\text{Se}$ heterointerfaces in the composite film can scatter short- to long-wavelength phonons because PPy has an intrinsic low thermal conductivity, the composite film has a low thermal conductivity.

Summary and prospects The functional unit order is an effective strategy to optimize the performance of materials. For Ag_2Se -based TE films, the TE functional units ordering (such as coherent adjacent Ag_2Se grains, good crystalline qualities, continuous grain boundaries, and core–shell nanostructure) and flexible functional units were constructed in Ag_2Se -based films. The effective regulation of electron and phonon transport and flexibility was realized due to the synergistic effect between different functional units, thus increasing the electrical conductivity, reducing the thermal conductivity, and improving the flexibility. The more work are needed to verify whether the relevant strategies are universal.

Keywords thermoelectric film; silver selenide; functional units ordering; flexible