二维过渡金属硫族化合物的研究进展

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摘要 二维过渡金属硫族化合物(transition metal dichalcogenides, TMDCs)是继石墨烯之后的新型范德瓦耳斯材料, 由于其天然的二维特性以及强自旋轨道耦合作用(spin-orbital coupling, SOC), 导致诸如金属-绝缘体转变、电荷密度波(charge density wave, CDW)、能谷电子学、非常规超导电性等新颖物理性质的出现, 使得这类材料成为研究低维量子物理的又一理想平台。其中能谷电子学与拓扑超导已经成为近年来凝聚态物理前沿研究的热点方向。本文在综述TMDCs材料的结构与基本物理性质的基础上, 重点介绍了最近发展的用于生长原子层厚度的TMDCs材料的熔盐辅助化学气相沉积方法、在Se掺杂的 $\text{MoSe}_x\text{Te}_{2-x}$ 薄膜中实现的 T_d 相到 $1T'$ 相再到 $2H$ 相的结构相变与超导增强现象, 以及在少层 $T_d\text{-MoTe}_2$ 中发现的非对称性SOC作用引起的类伊辛超导现象。最后, 展望了TMDCs材料的潜在应用与可能存在的拓扑超导。

关键词 二维过渡金属硫族化合物, 自旋轨道耦合作用, 化学气相沉积, 结构相变, 伊辛超导

2010年的诺贝尔物理学奖颁发给了海姆(Andre Geim)和诺奥肖洛夫(Konstantin Novoselov), 以表彰他们对石墨烯(graphene)研究的突出贡献^[1], 这迅速引发了人们研究新型二维材料的热潮。在石墨烯以及类石墨烯材料中, 由于层间采用较弱的范德瓦耳斯力结合, 因此这类材料也被称为范德瓦耳斯材料^[2]。石墨烯、黑磷、六方氮化硼(h-BN)与过渡金属化合物(氧化物、碳化物、氮化物、硫化物)等均属于这一类材料家族, 其中过渡金属硫族化合物(transition metal dichalcogenides, TMDCs)则被认为是范德瓦耳斯材料的典型代表。本文将结合我们最近的工作着重介绍二维过渡金属硫

族化合物的研究进展。

1 二维过渡金属硫族化合物的结构

典型的二维过渡金属硫族化合物化学式可以表示为 MX_2 , 其中M代表过渡金属元素(如钼Mo、钨W、铌Nb), X代表硫族元素(如硫S、硒Se、碲Te)等。由于过渡金属原子配位方式的不同, TMDCs存在多种结构相, 最常见的是三棱柱($2H$)和八面体($1T$)配位两种, 如图1(a)所示。这些不同结构来源于单层TMDCs内3个单原子层(X-M-X)的不同堆叠次序, $1H$ 相对应于ABA的堆积方式, 不同原子层的硫族原子始终占据相同的位置

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A, 在垂直于层的方向上, 每个硫族原子正好位于下层硫族原子的正上方; 而1T相对应于ABC的堆积方式. 一般认为1T相在热力学上不稳定, 过渡金属原子M会自发地发生扭曲, 形成一维锯齿(zig-zag)链, 转变为1T'相.

2H相与1T'相元胞对称性的不同导致了两种材料展现出截然不同的性质. 有意思的是, 这些不同的结构相不仅可以通过调节化学组分^[3](图1(b))的内在手段加以调控, 还可以通过应力场、温度场、电场、磁

图1 (网络版彩色)TMDCs的结构与组成^[3]. (a) 典型的层状过渡金属硫族化合物MX₂中3种常见的原子结构, 2H, 1T与1T'相. 需要说明的是, Fe基硫族化合物(如FeS与FeSe)的化学式为MX. (b) 层状过渡金属硫族化合物的不同元素结构、物理性质列表. FM, 铁磁; AFM, 反铁磁; S, 超导; CDW, 电荷密度波

Figure 1 (Color online) Structure and composition of TMDCs^[3]. (a) Three typical atomic structures of 2H, 1T and 1T' phase in layered transition metal dichalcogenides MX₂ (The structure of Fe-based chalcogenides like FeS and FeSe is MX). (b) Table for various 2D TMDCs and other 2D materials exhibiting various physical properties. FM: Ferromagnetism, AFM: antiferromagnetism, S: superconductivity, CDW: charge density wave

场、光场以及样品厚度等外在手段加以调控。这些调控手段为研究二维TMDCs的丰富物性提供了强有力的手段^[4-7], 如图2(a)所示。如2H相的体样品MoS₂是典型的间接带隙半导体^[8,9], 其能隙 $E_g \sim 1.29$ eV。伴随着厚度的减小, 能隙逐渐增大, 到单层时转变为直接带隙($E_g = 1.8$ eV)半导体^[8,9], 如图2(b)所示。更为重要的是, 晶格对称性以及自旋轨道相互作用带来的能谷简并与分裂, 开启了全新的能谷电子学^[10]。在此基础上, 谷霍尔效应^[11]、激子霍尔效应^[12]等新奇量子现象相继被发现。同时, 加压会导致MoS₂体样品发生绝缘体到金属的转变^[13], 而基于离子液体的电场调控则可以驱使单层MoS₂发生从绝缘体到超导体的转变, 超导转变温度达到了9.4 K^[14], 不仅如此, 其面内上临界磁场更是

超过了传统BCS理论预言的泡利极限, 需要用伊辛(Ising)超导理论来解释^[15]。另一方面, 理论(图2(c))预言在1T'相的单层TMDCs(如MoS₂、MoSe₂、MoTe₂和WTe₂等)材料中存在量子自旋霍尔效应^[16,17]。这一预言随后得到了角分辨光电子能谱(angle resolved photoemission spectroscopy, ARPES)^[18,19]与电学输运测量等实验上^[20,21]的支持, 如图2(d), (e)所示。除了量子自旋霍尔效应外, 1T'相的MoTe₂体样品会随温度发生相变, 在低温下转变为 T_d 相, 并在0.1 K出现超导^[22,23]。在厚度、缺陷、掺杂、加压、自旋轨道耦合作用等多方面的调制下, 在该体系内出现了多种相变和超导增强现象(图3(a))^[24-28], 以及拓扑超导^[23,29]、 S^+ 配对超导(图3(b))^[30,31]、各向异性超导^[32]等非常规超导现象。除

图2 (网络版彩色)TMDCs的丰富物性。(a) 二维TMDCs材料为研究二维情况下的伊辛模型、XY模型、海森堡模型等提供了理想素材^[6]。可以利用电场、光场、应力场、摩尔纹和临近效应等手段调控 $\pm K$ 处的能谷电子或边界态性质。(b) 2H-MoS₂能带简化图^[9]。(c) 1T'-MoS₂能带图, E_g 代表主能隙, 2δ 代表反转能隙^[16]。(d) 单层1T'-WTe₂角分辨光电子谱^[18]。(e) 单层1T'-WTe₂中观测到的量子自旋霍尔效应^[21]。左图: 单层1T'-WTe₂器件结构示意图、实物图以及4 K温度下电导随门电压的变化; 右图: 边缘态电导在不同门电压下随温度的变化曲线

Figure 2 (Color online) Various physical properties of TMDCs. (a) Two-dimensional Van der Waals materials offer an ideal platform to study the fundamental magnetism models^[6] (the Ising, XY, and Heisenberg model). Moreover, the valley electrons or edge states can be tuned by electric field, optical, strain, Moiré stripe and proximity effect. (b) Simplified band structure of 2H-MoS₂^[9]. (c) Band structure of 1T'-MoS₂. E_g is fundamental gap, and 2δ is inverted gap^[16]. (d) ARPES data of bandgap opening in monolayer 1T'-WTe₂^[18]. (e) Quantum spin Hall effect observed in monolayer 1T'-WTe₂^[21]. Left panel: schematic and optical image of monolayer 1T'-WTe₂ device and four-probe conductance measurement as a function of V_{lg} at 4 K. Right panel: Edge conductance as a function of temperature at different gate voltages V_c .

图3 (网络版彩色)TMDCs的相变与超导. (a) MoTe₂的温度-压力相图^[27]. (b) MoTe₂在1 GPa压力下穿透深度随温度的变化曲线^[31]. (c) 2H-TaSe₂的温度-压力相图^[40]. (d) 理论上实现拓扑超导的几种方案^[45]. (e) FeSe的晶格常数-温度相图^[44]. (f) FeTe_{0.55}Se_{0.45}样品在超导涡旋中心出现的马约拉纳(Majorana)零能模^[47]

Figure 3 (Color online) Phase transition and superconductivity of TMDCs. (a) Phase diagram of MoTe₂ plotted against temperature and pressure^[27]. (b) Temperature dependence of penetration depth for MoTe₂ at 1 GPa^[31]. (c) Phase diagram of 2H-TaSe₂ plotted against temperature and pressure^[40]. (d) Different proposals to realize topological superconductivity^[45]. (e) Phase diagram of FeSe plotted against temperature and lattice constant^[44]. (f) Caroli-de Gennes-Matricon bound states (CBSs) in a vortex with Majorana zero mode (MZM) in FeTe_{0.55}Se_{0.45}^[47]

了这些VI族过渡金属元素(Mo和W)形成的MX₂具有新奇的物理性质外, 在IV族和V族的过渡金属元素Ti、Zr、Hf、V、Nb、Ta等化合物中还出现了超导和电荷密度波(charge density wave, CDW)共存等现象^[33~41], 典型的结果如图3(c)所示; 值得说明的是, 有着VIII族元素的Fe基硫族化合物MX更是近期高温超导^[42~44]和拓扑超导^[45~48]研究的热点内容. 图3(d)~(f)展示了铁基超导研究的最新进展, 包括FeSe块体到薄膜变化的相图^[44]、Fe(Te, Se)系统中可能实现拓扑超导的多种方案^[45]以及在FeTe_{0.55}Se_{0.45}样品的磁通涡旋中发现的马约拉纳(Majorana)零能模和可以区分磁通涡旋所处拓扑状态的Caroli-de Gennes-Matricon束缚态(CBSs)等现象^[47]. 除了在上述基础研究领域的优势外, 二维过渡金属硫族化合物还展现出广泛的器件应用前景^[3,49]. 如基于二维半导体TMDCs的场效应晶体管^[50]、光电器件^[51,52]、压电器件^[53,54]、柔性器件^[55]已经在能量储

存^[56]、电催化^[57]等领域表现出优异的性能; 而基于二维半金属TMDCs的非常规超导器件^[58,59], 则为下一代拓扑量子计算提供了新的实验平台. 因此, 二维TMDCs已经成为近年来凝聚态物理与材料科学研究的热门方向. 接下来本文将从二维TMDCs的制备方法、物性测量以及新型器件的设计等方面加以系统介绍.

2 二维过渡金属硫族化合物的制备

近年来, 随着对二维材料研究的不断深入, 高质量的薄层甚至单层结构的制备变得愈加迫切. 现有的二维TMDCs制备方法主要分为“自上而下”的剥离法(解理)与“自下而上”的合成法两类^[60].

由于层状TMDCs层间采用范德瓦耳斯力结合, 在外力的作用下容易分离, 因此可以利用“自上而下”的剥离法获得少层或单层TMDCs材料, 其中主要包括超声液相剥离法^[61]、插层剥离法^[62]、机械剥离法^[1,63]等.

超声液相剥离法与插层剥离法(图4(a))具有较高的产率,可以用于工业生产,在能量储存、催化、电容器件等方面展示出良好的应用前景.在基础研究领域,由于对器件的质量要求较高,机械剥离法是当前更为常用的手段.机械剥离法源于Geim和Novoselov^[1]利用胶带从石墨中解理出单层石墨烯的操作.通过选择一定黏性的胶带、控制合理的解理温度,以及合适的衬底材料,经过反复多次减薄,可以解理出百微米级别甚至更大面积的单层石墨烯样品(图4(b))^[63].此外,整个解理过程可以在手套箱内完成,从而有效防止了样品氧化,这样得到的样品具有很高的质量^[64].为了进一步提高样品质量,人们最近发展了固相转移技术^[65,66],通过聚二甲基硅氧烷(PDMS)膜将六方氮化硼(h-BN)和二维TMDCs薄膜精确定位,并叠放到一起形成三明治结构^[67,68].通过这种搭积木的方式,人们可以自由地设计电极与异质结结构^[69~73],为未来器件的设计提供了无限可能.利用该方法已经实现了衬底+背门电极+氮化硼介电层+样品+电极+氮化硼介电层+顶门这样7层的复杂结构(图2(e)),在100 K高温下实现了量子自旋霍尔效应^[21],而且这种技术经过改良还可以转移电极、改善接触,进一步提高器件性能^[72](图4(c)).这些新型器件的制备方法表现出强大的可操作性,并且极大地拓展了二维器件的功能.

通常情况下,采用剥离法所得到的材料尺寸较小.为了获得更大尺寸的二维TMDCs材料,人们发明了“自下而上”的方法,主要包括分子束外延(molecular beam epitaxy, MBE)法^[74]、化学气相沉积(chemical vapor deposition, CVD)法^[75]、水(溶剂)热合成法^[76]、胶体合成法^[77]等.这里我们主要介绍前两种比较常用的方法.利用MBE方法可以生长出质量较好的二维TMDCs^[78~80]和h-BN^[81~83]等材料.但是成本太高,而且自由度受限,一台MBE只能生长特定元素的材料,否则会交叉污染,影响样品质量.与之相对,CVD技术具有设备简单、成本低廉、灵活性高的优势,但是通常得到的材料质量与MBE生长的样品有一定的差距.

有鉴于此,我们发展并完善了一种普适性的熔融盐辅助化学气相合成策略^[84],如图5(a)~(c)所示.该方法的核心思想是通过引入熔融盐有效降低金属前驱体的熔点,从而使得前驱体具有较高的质量流量,参与形核与反应;与此同时,熔盐与某些金属氧化物前驱体反应形成的卤氧化物促进了二维TMDCs的生长.采用此方法可以生长出包括通常方法难以合成的铌(Nb)基、

铂(Pt)基、钛(Ti)基在内的47种原子级厚度的TMDCs材料,涉及12种过渡金属元素(Ti、Zr、Hf、V、Nb、Ta、Mo、W、Re、Pd、Pt、Fe)和3种硫族元素(S、Se、Te).样品涵盖了两元、三元、多元和异质结材料.通过控制不同前驱体的流量以及生长速率,不仅可以得到大面积的单层单晶薄膜(毫米级),也可以得到几十微米大小、形状规则的独立单层单晶结构,非常适合开展单层TMDCs的器件研究.

这里以生长少层MoTe₂为例,简要介绍熔融盐辅助化学气相合成方法的原理及过程.图5(a)给出了样品生长的实验装置示意图.整个反应过程是在直径为1 in(1 in=2.54 cm)的石英管中进行的,装有前驱体粉末(NaCl:MoO₃=1:5)的氧化铝舟放在石英管中央,SiO₂/Si基片放置在氧化铝舟的正上方,同时保持基片正面向下;另一个装有Te粉的氧化铝舟放置在石英管的上游,并使其恒温在450°C,反应过程中通以H₂/Ar(流量为15/80 sccm)作为载气.反应时,以50°C/min快速升温至700°C并维持4 min,然后自然降温即可得到少层MoTe₂样品.如图5(b)所示,在生长过程中,熔盐的引入一方面有效地降低了金属前驱体的熔点,另一方面它可以与MoO₃反应形成易于蒸发的金属氯氧化物(MoO_xCl_y),促进MoTe₂的生长.从图5(c)可以看出,当金属前驱体质量流量较大时,倾向于生长成单层多晶薄膜;而当金属前驱体质量流量较小时,较易生长成结构规则的单层单晶.

为了表征利用上述方法合成样品的质量,我们在单层NbSe₂样品上利用微纳加工技术制备了霍尔条(Hall bar)器件,得到了良好的结果^[85].图5(d-i)给出了零磁场下,单层NbSe₂样品的纵向电阻随温度的变化曲线($R_{xx}(T)$).很明显,在高温时,样品呈现出金属性导电行为($dR/dT>0$).当温度进一步降低时,单层NbSe₂在1.5 K时 R_{xx} 开始急剧下降,当温度达到0.8 K时,样品达到了零电阻态,表明样品发生了超导转变.除此之外,我们发现样品的超导转变温度 $T_c(0R_N)$ (定义为样品进入零电阻态时对应的温度)随着样品厚度的降低而降低,从10层厚样品的4.56 K降至5层厚样品中的4.2 K,进而降至单层样品中的0.8 K.需要说明的是,我们利用熔盐辅助CVD法生长的单层NbSe₂样品的超导转变宽度(ΔT_c)仅有约0.7 K,小于目前所有MBE样品中报道的结果^[86,87],可以与机械剥离得到的最好样品相比^[88].这说明利用熔盐辅助法生长的样品具有非常高的质量,可以用于基础研究.

通过进一步测量上临界磁场 H_{c2} 与不同温度下电

图4 (网络版彩色)TMDCs样品的解理制备方法。(a) 锂离子插层剥离法制备单层TMDCs流程示意图^[62]。(b) 使用胶带解理二维材料的机械剥离法操作图以及获得的大面积石墨烯样品^[63]。(c) 基于接触电极转移(TVCs)和传统固相转移技术的器件制备流程^[72]。
Figure 4 (Color online) Exfoliation methods of TMDCs samples. (a) Schematic illustration of electrochemical lithiation intercalation exfoliation for production of monolayer TMDCs^[62]. (b) Illustration of the modified exfoliation process for layered crystals and the optical image of large-area graphene flakes^[63]. (c) Device fabrication process based on transferred via contacts (TVCs) and conventional dry-transfer method^[72].

流-电压特性曲线 $I(V)$ ，证明了这些单层的NbSe₂为二维超导体。图5(d-ii)给出的是不同外加垂直磁场下的 $R_{xx}(T)$ 曲线。随着外加磁场的不断增强，超导转变温度逐渐向低温方向移动，最终在1.5 T的外加磁场下超导被完全抑制。图5(d-iii)给出了单层NbSe₂的 $H_{c2} \sim T_c$ 相图。显然， H_{c2} 与 T 之间满足线性依赖关系，这是二维超导体的典型特征^[89-91]。它可以用标准的Ginzburg-Landau(GL)理论解释， $H_{c2} = \frac{\phi_0}{2\pi\xi_{GL}} \left(1 - \frac{T}{T_c}\right)$ ，其中 ξ_{GL} 为零温下GL相干长度， ϕ_0 是磁通量子。利用上式对 $H_{c2}(T)$ 加以拟合，可以得到 $\xi_{GL}(0)=18$ nm。由此可见， $\xi_{GL}(0)$ 远大于单层样品的厚度(~ 1.0 nm)，所以它是二维超导体。上述结论也可以通过测量Berezinskii-Kosterlitz-Thouless(BKT)转变^[92]来证实。图5(d-iv)是在不同温度下测量的电流-电

压特性曲线($I \sim V$)。随着温度的降低，我们发现 $I \sim V$ 曲线由线性行为转变为幂指数行为 $V \propto I^\alpha$ ，这符合BKT理论对二维超导体的预期。类似地，我们也证明了少层1T_d-MoTe₂是典型的二维超导体^[32]。值得一提的是，这是首次在CVD合成的单层样品中实现的超导电性^[93]。

由此可见，熔融盐辅助化学气相沉积方法是一种获得高质量的二维TMDCs的有效手段。它极大地提高了材料学研究的效率，为开展二维TMDCs的研究提供了理想素材。

3 二维过渡金属硫族化合物的物性

3.1 能谷电子学

传统的半导体器件利用电子的电荷属性来进行信

图 5 (网络版彩色)熔融盐辅助化学气相沉积法生长高质量TMDCs材料^[84]. (a) 实验装置示意图. (b) 反应机制示意图与典型样品. (c) 不同条件的生长过程示意图与典型样品. (d) 使用该方法生长的高质量单层NbSe₂二维超导体的输运结果^[85]
Figure 5 (Color online) Growth of high-quality TMDCs with melt-salt-assisted chemical vapor deposition method^[84]. (a) Schematics illustration of experimental setup. (b) Schematics of reaction mechanism and optical images of typical samples. (c) Flow chart of the general growth process in different conditions and optical images of typical samples. (d) Transport characterizations of two-dimensional superconductivity in monolayer NbSe₂^[85]

息处理和传输. 除此之外, 固体中的电子还有自旋和能谷两种自由度. 近年来随着对自旋和自旋器件研究的深入, 逐渐形成了自旋电子学(Spintronics)这一分支. 最近, 在具有特殊对称性的二维TMDCs中出现了将布洛赫(Bloch)电子的能谷作为新颖自由度的研究, 它开启了能谷电子学(Valleytronics)新方向. 能谷指的是布洛赫电子能带的极值点(导带底或价带顶), 其中占据的电子就是能谷电子. 研究这些简并但不等价的电子自由度, 调控其中电子的状态、改变拓扑性质, 通过磁、光、电等手段编码存储信息等构成了能谷电子学的主要研究内容^[94-98]. 在二维材料出现之前, 多能谷半导体材料并不理想, 直到石墨烯以及二维TMDCs出现以后, 能谷电子学才有了理想的研究平台^[10]. 这类材料在布

里渊区边缘有着不等价的 $+K$ 和 $-K$ 能谷, 类似于二能级系统或者自旋1/2的系统^[99,100], 不同能谷之间的自旋磁矩可能给出能谷极化, 导致如图6(a)所示的磁化现象. 同时, 这两个由对称性破缺产生的能谷对圆偏振光具有选择性的吸收, 如图6(c)所示, 在单层WSe₂中, 左旋和右旋泵浦光产生出相反克尔旋转信号, 表现出选择性吸收的特点, 也证实系统中出现的快激子谷极化现象^[101]. 因此, 基于圆偏振光的谷极化^[102-106]是调控谷电子的有效手段之一. 此外, 谷霍尔效应(valley Hall effect, VHE)^[100,107]也是能谷电子的独特性质. 由对称性破缺导致的有限贝里曲率在两个能谷之间符号相反, 其充当的有效磁场使得不同能谷间的电子受到了方向相反的作用, 在给面内电场的情况下, 不同能谷之间

图6 (网络版彩色)TMDCs中的谷电子学。(a) 单层MoS₂中由能谷极化(i)、无能谷极化(ii)以及应力下电流(iii)导致的磁化^[97]。(b) 电场(i)与光场(ii)驱动下的能谷霍尔效应与能谷的光跃迁选择定则(iii)^[100]。(c) 在4 K温度下, 使用左旋(σ^+)和右旋(σ^-)泵浦光产生的克尔旋转(Kerr rotation)信号^[101]。(d) MoS₂器件中由线偏振光产生的关于谷霍尔效应的克尔旋转信号^[108]。(e) 单层MoS₂中的(逆)谷霍尔效应^[109]。(f) 逆谷霍尔效应产生的非局域电压信号^[109]

Figure 6 (Color online) Valleytronics of TMDCs. (a) Magnetization with (i) and without (ii) valley polarization, and current-induced (iii) magnetization in the strained monolayer MoS₂^[97]. (b) Valley Hall effects (VHE) driven by electric (i) and optical (ii) field, and valley optical transition selection rules (iii)^[100]. (c) Kerr rotation dynamics at $T = 4$ K for a σ^+ and σ^- pump beam in WSe₂^[101]. (d) Kerr rotation image of the VHE in MoS₂ by linearly polarized light^[108]. (e) Schematic of valley-coupled topological current due to VHE and inverse VHE (iVHE)^[109]. (f) Measured nonlocal voltage corresponding to iVHE^[109]

的电子就会朝相反的方向运动, 积累在样品边缘。因此, 即使在没有外加磁场的情况下, 电子也出现了垂直于电场方向的运动, 这就是谷霍尔效应(图6(b))。在光学实验上, 双层MoS₂晶体管中测到的在样品两个边缘符号相反克尔信号(图6(d))反映出VHE导致的谷极化电流在空间中的分布, 直观地表明VHE的存在^[108]。在输运实验上, 单层MoS₂霍尔条器件中测到非局域霍尔电压(图6(e), (f)), 证实了系统中由谷霍尔效应产生的谷电流传输^[109,110]。除此之外, 该类材料中的谷激子由于增强的库仑作用变得更加稳定, 表现出很强的光学响应(图6(c)), 在能谷电子学器件的光场调控上扮演了重要的角色^[101,111~114]。通过磁场、电场、光场控制能谷电子极化, 谷激子产生和转移, 有望实现信息的写入和

读出, 从而开发出基于能谷电子学的半导体器件^[115,116]。

3.2 相变与两带超导

二维TMDCs中结构相的多样性^[117]带来了丰富的材料性质^[118]与调控手段^[119~121], 同时也导致了众多新奇的物理现象, 比如单层2H相中的伊辛超导^[15,89]、单层1T相中的量子自旋霍尔效应^[16~21]以及少层T_d相中的非对称性自旋轨道耦合作用导致的类伊辛超导^[32]等。因此, 如果能够找到一种有效的调控方法可以使少层TMDCs在2H相、1T相、T_d相之间连续变化, 那么就有可能在同一种材料中通过整合超导与量子自旋霍尔效应实现人们期待已久的本征拓扑超导。另一方面, 相工程(phase engineering)研究也为二维TMDCs在电子学器

件、光电器件、能谷电子学器件以及电催化等方面的潜在应用奠定了基础^[122,123]。

在上述思路的指引下,我们开展了通过Se的掺杂来实现少层MoTe₂中从 T_d 相到 $1T'$ 相再到 $2H$ 相转变的研究^[124]。在此之前,人们仅在少层TMDCs中通过加热^[22,30,125,126]、维度^[24]、元素掺杂^[127,128]、化学修

饰^[129,130]、激光辐照^[131]、应变^[27,28,132]以及电场^[133]等调控手段实现了 $2H$ 相到 $1T'$ 相或 T_d 相到 $1T'$ 相的转变。而我们基于MoSe_xTe_{2-x}薄膜的工作是首次在少层TMDCs中实现了这3个相之间的连续转变。图7(a)给出了利用熔融盐辅助CVD法生长的高质量MoSe_xTe_{2-x}样品的光学照片。通过调节生长温度、生长时间,以及Se和Te前

图 7 (网络版彩色)MoSe_xTe_{2-x}中的相变与两带超导^[124]。(a) 少层不同结构相MoSe_xTe_{2-x}样品的光学照片。(b) MoSe_xTe_{2-x}薄膜样品随Se取代量 x 变化的拉曼光谱。(c) MoSe_xTe_{2-x}薄膜样品从 T_d 到 $1T'$ 再到 $2H$ 相转变的晶格结构变化示意图。(d) MoSe_xTe_{2-x}薄膜样品的相图。(e) MoTe₂和MoSe_{0.95}Te_{1.05}薄膜样品中上临界场的单带WHH模型与两带模型拟合结果

Figure 7 (Color online) Phase transition and two band superconductivity in MoSe_xTe_{2-x}^[124]. (a) Optical images of different phases in few-layer MoSe_xTe_{2-x}. (b) Raman spectra of MoSe_xTe_{2-x} with different x . (c) Schematic of phase evolution from T_d to $1T'$ to $2H$ in MoSe_xTe_{2-x}. (d) Phase diagram of MoSe_xTe_{2-x} thin film samples. (e) The fitting results of upper critical field with the WHH and two-band model in MoTe₂ and MoSe_{0.95}Te_{1.05} thin films

驱体粉末的比例实现了对厚度、结构相以及Se含量的有效控制。图7(b)是拉曼光谱随着Se掺量的演化行为,其中Se的掺量是通过X射线光电子能谱(X-ray photoelectron spectroscopy, XPS)确定的。纯 MoTe_2 ($x=0$)中95、113、131与163 cm^{-1} 处的拉曼谱特征峰对应于 T_d 相 MoTe_2 中的 A_1 与 A_2 振动模。当引入Se原子后,113和131 cm^{-1} 的拉曼谱特征峰发生了明显的红移。随着Se掺量由0.3增加到0.8,与纯 MoTe_2 相比,结合扫描透射电子显微镜(scanning transmission electron microscopy, STEM)数据^[124],发现当 x 接近0.8时,样品所有拉曼谱特征峰发生了明显的蓝移,已经由 T_d 相转变到 $1T'$ 相。当 x 超过0.9时,新出现的 E_{1g} (122 cm^{-1})与 A_{1g} (122 cm^{-1})拉曼谱特征峰对应于 $2H$ 相的出现。上述相转变过程得到了XPS数据的进一步支持^[123]: $x<0.7$ 时,是正交的 T_d 相; $0.7<x<0.8$ 时,体系处于 T_d 相与 $1T'$ 相的混合相;在 $0.8<x<1.0$,是单斜的 $1T'$ 相; $x>1.0$ 以后是 $2H$ 相。图7(c)给出了其结构演化过程。此外,通过电学输运测量的手段也证实了该体系的导电行为的确从金属转变到了半导体,如图7(d)所示。随着Se掺量的增加,室温面电阻 R_s 急剧上升了4个量级,表明体系发生了金属-绝缘体转变。综上所述,通过对Se掺量的精确控制,我们在少层 $\text{MoSe}_x\text{Te}_{2-x}$ 中实现了从 T_d 相到 $1T'$ 相再到 $2H$ 相的连续调控。有意思的是,我们从图7(d)中发现,随着Se掺量从0增加到1.0, T_c 从2.1 K单调增加到了3.6 K,表明Se的掺杂增强了超导性。为了理解超导增强的机制,我们利用Bloch-Grüneisen^[134]公式对正常态的电阻-温度曲线进行了拟合,得到了样品的德拜温度 θ_D 。进而结合麦克米兰(Macmillan)^[135]公式计算了电-声子耦合常数 λ ,发现不同掺杂样品的 λ 均在0.65附近,表明样品属于弱耦合的BCS超导体。相比于块体样品中的 $\lambda\sim 0.31$ 来说,薄膜样品的电-声子耦合常数明显增大,这很好地解释了薄膜样品中 T_c 均比体样品高的原因。但是随着Se含量的增加, λ 基本保持不变,这无法解释实验上观测到的 T_c 随Se含量的增加而升高的现象,需要做进一步分析。

近来,人们在S/Se掺杂和物理加压两种条件下的 MoTe_2 体样品中观察到类似的超导增强现象,以及非平庸超导^[28,29]与两带超导^[30,31]特征。在我们的体系中,由于采用了离子半径较小的 Se^{2-} (1.98 Å)取代较大的 Te^{2-} (2.21 Å),因此也存在化学压力,可能与S/Se掺杂或加压的 MoTe_2 具有相同的超导增强机制。为此,我们详细测量了面外上临界磁场与温度的依赖关系 $H_{c2,\perp}(T)$,如图7(e)所示。从图中可以看出,对于少层纯 MoTe_2 样品,

单带S波理论模型(Werthamer-Helfand-Hohenberg model, WHH model)^[136]可以很好地描述 $H_{c2,\perp}(T)$,表明少层的 MoTe_2 是通常的S波超导体。但对于少层 $\text{MoSe}_{0.95}\text{Te}_{1.05}$ 样品而言,WHH模型不能很好地拟合实验数据,尤其是低温下(<1 K)明显与实验结果偏离。相比之下,两带超导模型^[137]能很好描述整个温区的 $H_{c2,\perp}(T)$ 曲线行为,表明 $\text{MoSe}_{0.95}\text{Te}_{1.05}$ 体系很可能是 S^+ 配对的两带超导体。

3.3 伊辛超导与非对称性自旋轨道耦合作用导致的类伊辛超导

在二维TMDCs中,除了刚刚提到的两带超导以外,还出现了其他新颖的非常规超导现象。因为这类体系中有较强的自旋轨道耦合作用,使得能带电子的行为发生了很大的变化。在单层 $2H$ 相的TMDCs中,强自旋轨道耦合相互作用及面内对称性破缺导致了垂直样品表面的等效磁场产生^[138]: $H_{SO} \propto k \times \varepsilon$,如图8(a)所示。与通常的Rashba型的自旋轨道相互作用导致的结果不同,该等效磁场指向面外(图8(b)),而且理论计算表明这个有效磁场高达几百特斯拉,远远超过现有实验室所能获得的最高磁场。在如此强的磁场作用下,电子的自旋被牢牢地锁定在面外方向,从而使得面内磁场很难改变自旋方向。因此这种电子结成库伯对之后,可以承受非常强的面内磁场而不发生失超,表现为面内上临界磁场($H_{c2,\parallel}$)显著增强,这种现象被称为伊辛超导^[58]。目前,人们已经在离子门调控的单层 $2H\text{-MoS}_2$ ^[15,139]、单层 $2H\text{-NbSe}_2$ ^[89,140,141]、单层 $2H\text{-WS}_2$ (图8(c))^[142]等单层TMDCs中发现了伊辛超导。在各种实验中测量到的 $H_{c2,\parallel}$ 均远高出BCS常规超导体泡利极限: $H_P = \sqrt{2} \Delta_0 / (g\mu_B)$,如图8(d)所示,这是伊辛超导的典型特征。

从伊辛超导的机制可以看出,对称性破缺与强自旋轨道耦合作用是产生伊辛超导的必要条件。只要满足以上两点,这种面内上临界场增强的现象就不只局限于单层 $2H$ 相六角结构的样品中。最近,我们在少层的 T_d 相 MoTe_2 样品中,也发现了与伊辛超导类似的 $H_{c2,\parallel}$ 增强现象^[32],如图9(a)所示。不同的是, $H_{c2,\parallel}$ 在不同面内旋转角(φ 定义为面内磁场与 y 轴正半轴方向的夹角)展现出明显的各向异性(图9(c)),而且随着 φ 的变化呈现出两重对称性,如图9(d)所示。这无法用现有的伊辛超导理论来解释,因为单纯的面外等效磁场 H_{SO} 只能产生各

图8 (网络版彩色)TMDCs中的伊辛超导。(a)伊辛超导原理示意图^[138]。(b)外加磁场对于Rashba型和塞曼型有效背景下的库珀对的影响效果示意图^[15]。(c)离子门调控的 WS_2 样品超导转变的拱形相图^[142]。(d)不同材料的上临界场随温度的变化曲线^[142]。
Figure 8 (Color online) Ising superconductivity of TMDCs. (a) Schematic of Ising superconductivity^[138]. (b) Interplay of an external magnetic field and the spins of Cooper pairs aligned by Zeeman and Rashba-type effective magnetic fields^[15]. (c) Phase diagram of ion-gated monolayer WS_2 ^[142]. (d) Normalized upper critical fields with respect to Pauli limit in different materials^[142].

向同性的 $H_{c2\parallel}$ 。上述的两重对称性还体现在超导临界电流 I_c 上,如图9(e)所示。从中可以清楚地看到,不同磁场下的 I_c 随着面内旋转角 ϕ 也呈现出两重对称性。需要说明的是,这种新奇的各向异性输运性质(由 $H_{c2\parallel}(0^\circ)/H_{c2\parallel}(90^\circ)$ 的比值来表征)仅在少层样品中出现,并且随着样品厚度从4 nm增加到9 nm,该比值从1.56下降到1.16,表明两重对称性是少层 T_d 相样品的特有行为。

为了深入理解上述奇异的输运行为,我们与理论合作者以双层 T_d 相 $MoTe_2$ 为研究对象,从对称性的角度

出发,建立了有效模型。图9(b)给出了双层 T_d 相 $MoTe_2$ 的晶体结构示意图,它仅在y轴方向上具有镜面对称性,而在x轴方向与面外方向上均发生镜面对称破缺。考虑到时间反演对称性与y轴方向上的镜面对称性,双层 T_d 相 $MoTe_2$ 中的有效自旋轨道耦合作用可以表示为 $H_{SO} = g \cdot \sigma$,⁽¹⁾其中 $g = (g_x, g_y, g_z)$ 为自旋轨道耦合作用。在双层 T_d 相 $MoTe_2$ 中,x轴方向的镜面对称破缺产生了面外的伊辛自旋轨道耦合作用 g_z ,而面外的镜面对称破缺产生了

图 9 (网络版彩色)非对称性自旋轨道耦合作用导致的类伊辛超导^[32]. (a) 不同厚度样品的面内上临界场. (b) T_d 相 MoTe_2 样品的面内结构及对称性示意图. (c) 不同面内旋转角下的超导转变. (d) 面内上临界场的两重对称性. (e) 不同面内磁场下, 临界电流对旋转角的两重对称性. (f) 不同面内方向的自旋磁化率计算结果. (g), (h) 分别是 y 和 x 方向面内上临界场随温度的变化

Figure 9 (Color online) Asymmetric spin-orbit coupling induced ising-like superconductivity^[32]. (a) In-plane upper critical fields with different thickness. (b) Schematic of crystal in plane structure and symmetry. (c) Field-dependent sheet resistance at different in-plane tilt angles. (d) Two-fold symmetry of in-plane upper critical field. (e) Two-fold symmetry of critical current under in-plane field. (f) Temperature dependence of the normalized in-plane spin susceptibility along different directions. (g), (h) The temperature phase diagram for the superconducting state with anisotropic SOC under y - and x -oriented in-plane magnetic field, respectively

面内各向异性的面内自旋轨道耦合作用 g_x 与 g_y . 因此, 在双层 T_d 相 MoTe_2 中同时存在 g_x 、 g_y 与 g_z , 这一点与已知的伊辛超导体明显不同. 与 $2H$ 相TMDs类似, g_z 对 $H_{c2,||}$ 具有显著的增强效应. 而面内各向异性的 g_x 与 g_y , 导致了面内上临界场与临界电流等物性的两重对称性.

为了定量地描述这种非对称性的自旋轨道耦合作用, 我们的合作者分别计算了面内自旋磁化率:

$$\frac{1}{2}N_0A_0^2 + \frac{1}{2}\chi_S H_{||}^2 = \frac{1}{2}\chi_N H_{||}^2, \quad (2)$$

其中 χ_S 与 χ_N 分别代表超导态与正常态的自旋磁化率, N_0 代表费米能级处的态密度. 图9(f)给出了考虑自旋轨道耦合作用后, x 轴与 y 轴两个方向上的自旋磁化率. 从图9(f)的插图可以清楚地看出 χ_{xx} 与 χ_{yy} 具有明显的各向异性. 又因为 $H_{c2,||}(\varphi) = \sqrt{N_0/(\chi_N - \chi_S)} A_0$, 由此可以得出

不同方向的面内上临界场, 如图9(g), (f)所示, 这也就解释了实验上观测到的 $H_{c2,||}(\varphi)$ 的两重对称性. 在图9(d)中, 实线是理论计算给出的绝对零温下的面内上临界磁场结果, 可以看出它与实验上在 $T=0.07T_c$ 时测量到的面内约化上临界磁场($H_{c2,||}(\varphi)/H_p$)结果十分吻合. 这表明非对称性的自旋轨道耦合作用是 $H_{c2,||}(\varphi)$ 增强及呈现两重对称性的原因. 这是在实验上首次观察到面内各向异性的类伊辛超导电性. 这一发现将有助于加深对过渡金属硫族化合物中新奇超导现象的认识, 促进相关材料超导自旋电子学器件上的应用研究.

4 二维过渡金属硫族化合物的应用

随着近年来集成电路对器件集成度的要求越来越高, 器件尺寸也相应越来越小; 同时为了适应器件的柔

性、轻薄、低功耗等新的功能需求,突破传统硅基器件瓶颈的新材料、新器件亟待发展起来.以石墨烯为代表的二维材料家族引起了人们的广泛关注,但由于石墨烯是零能隙的半金属,极大地限制了它在以半导体为基础的电子工业方面的应用.相比之下,二维过渡金属硫族化合物具有更为多样的晶体结构以及更丰富的物理性质,随着其合成技术的进步^[143,144],各种不同结构、功能的新型器件^[145-148]已经陆续出现.因此,二维TMDCs材料有望超过石墨烯实现更为广泛的应用前景^[149-152].

4.1 新型场效应晶体管

晶体管是现代电子工业的基础,而发展到今天,随着摩尔定律逐渐失效,硅基晶体管已经快要触及天花板了,因此基于二维TMDCs的新型场效应晶体管(field effect transistor, FET)有望成为新一代的基本元件.早期基于WSe₂的FET已表现出很高的电子迁移率^[153].在改善绝缘层工艺之后,基于MoS₂的FET的开关比达到了 $10^7 \sim 10^8$ 量级,迁移率也达到了数百 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ 的量级^[8,154].除了这类传统的场效应晶体管,最近人们利用干法转移技术制备了基于TMDCs材料的范德瓦耳斯异质结新型场效应晶体管^[155].这种类型的场效应晶体管不同于传统的金属-绝缘体-半导体的场效应晶体管,它通过整合不同导电性能的二维材料,借助原子级平整的二维平面,可以堆叠组合出功能各异的器件^[71,156].

将高导电率的石墨烯作为电极材料与半导体型的TMDCs组合成异质结,可以获得良好的欧姆接触,从而避免一般金属作为电极材料产生的肖特基势垒^[157,158].而二维氮化硼绝缘性能优异,并且可以解理出完美的平整表面,以它作为绝缘层可以极大地减少对沟道材料的破坏,以及对载流子的散射作用^[159].将这类范德瓦耳斯异质结应用到隧穿场效应晶体管上后(图10(a)),有望实现超低的漏电流、陡峭的亚阈值摆幅,以及超高的开关电流比的低功耗电子器件^[160,161].为了获得理想的工作性能,在实际应用中,应根据隧穿势能 E_{barr} 的不同选择合适的材料.如WSe₂/MoS₂异质结晶体管的 E_{barr} 偏大,不利于应用.后续研究将MoS₂替换为SnSe₂后, E_{barr} 降低到0.4 eV^[160];进而采用WS₂/SnS₂异质结后隧穿势降至0.02 eV,同时具有高达 10^6 量级的开关比,是比较理想的异质结器件^[162].除了平面结之外,还可以利用p型和n型的二维TMDCs堆叠成垂直结,实现了良好的整流特性^[163].除此之外,人们利用半导体型的

TMDCs材料开发了一种特殊的结型场效应晶体管(junction field effect transistor, JFET),它由p型MoTe₂和n型MoS₂组成^[164].它们互为另一材料的门电极和沟道,具有容易饱和以及高迁移率的优势.

由此可见,基于二维TMDCs的场效应晶体管不仅在基本性能上接近了传统的硅基器件,而且基于范德瓦耳斯异质结的器件更是表现出了传统器件所不具备的独特优势,为下一代高性能低功耗的电子器件打下了基础.

4.2 基于光电、储能、压电等特性的器件

半导体型过渡金属硫族化合物材料的能隙覆盖了从红外到深紫外的光谱范围(图10(b)),因此在光学上具有广泛的应用前景^[3,165].早在2011年,人们就发现基于单层MoS₂的光电器件性能要优于石墨烯器件^[166],而基于Ag/MoSe₂/SiO₂异质结的光探测器可以达到 10^{10} 琼斯的探测率以及微秒量级的响应时间^[167],如图10(c)所示.

在储能器件方面,利用石墨烯/MoS₂纳米片制备的复合材料作为负极材料(图10(d)),在很大的电流密度下依然具有相当高的比容量和良好的循环特性^[168].基于MoS₂的超级电容也是储能器件的新方向,其巨大的比表面积和层间空间使得MoS₂电极材料具有传输电子能力快与高电容^[169]等优势.

在压电器件方面,转移到PET柔性基底上的单层MoS₂具有明显的压电效应,0.53%的形变可以产生15 mV和20 pA的输出信号,表现出良好的压电性能^[170].此外,基于压电效应的二维TMDCs光探测器与气体探测器表现出良好的应用潜力^[54,171-173].目前,这两类原型器件已经在单层MoS₂上实现了.其核心思想是通过引入压电效应达到改变肖特基势垒和能带结构^[54]的目的.一方面,它使得光照条件下正负电荷的分离与传输更加容易实现^[172],可以明显提高光探测器的探测能力;另一方面,它能显著地改变吸附气体分子后的导电状态^[173],因而可以极大地提高气体探测器的工作性能.

4.3 柔性电子器件

由于二维TMDCs具有优异的机械性能和电学特性,因此在可穿戴的生物传感器、医学工业、折叠显示器、仿生器材、柔性机械等方面有着可观的应用前景^[55,147,148,174].最近研发的基于MoS₂的柔性晶体管^[56]表现出良好的机械性能,在经历了反复折叠后仍具有足够高的迁移率与开关比,达到了应用的基本要求.随

图 10 (网络版彩色)TMDCs的器件应用。(a) MoS₂/WS₂范德瓦耳斯异质结形成的p-n器件以及电流-电压特性曲线^[163]。(b) 从深紫外到红外光范围的二维材料的带隙大小示意图^[3]。(c) Ag/MoSe₂/SiO₂异质结光探测器示意图以及光电电压响应曲线^[167]。(d) 垂直生长在石墨烯上的MoS₂薄膜作为电极材料的锂离子扩散通道^[168]。(e) 在PI柔性薄膜上制备的MoS₂电子器件以及柔性逻辑电路的实物器件图^[175]。(f) 基于MoS₂的柔性Wi-Fi频段整流天线器件^[177]。(g) 基于高迁移率MoS₂薄膜晶体管的AMOLED柔性显示阵列^[179]

Figure 10 (Color online) Applications of TMDCs. (a) Schematic of a MoS₂/WS₂ heterojunction device and its current-voltage curves^[163]. (b) Bandgap of TMDs varying from ultraviolet to infrared^[3]. (c) Schematic of the Ag/MoSe₂/Si heterojunction photodetector and the photoresponse curve^[167]. (d) Schematic of paths for Lithium-ion diffusion in the MoS₂/G composite electrode^[168]. (e) Schematic of the device on PI films and optical image of rollable logic circuits^[175]. (f) MoS₂-based flexible rectenna for Wi-Fi-band wireless energy harvesting^[177]. (g) Flexible AMOLED display devices based on high mobility MoS₂ thin-film transistor^[179]

后, 基于MoS₂柔性逻辑电路的非门(NOT)和与非门(NAND)器件(图10(e))^[175]、RF电路器件^[176]、Wi-Fi频段的整流天线器件(图10(f))^[177]、反双极性晶体管器件^[178]相继被制造出来, 为进一步构建复杂的逻辑电路以及功能电路器件打下了基础。

此外, 使用MoS₂薄层晶体管TFT的AMOLED柔性显示器(图10(g))表现出良好的性能^[179]。在9 V门电压的情况下最大亮度可达408 cd m⁻², 响应时间2.5 ms; 而基于MoS₂的柔性非易失性存储器件^[180]在放置10 d之后, 可重写的内存依然具有超过10⁴大小的电阻比, 可重复性高达10⁴次循环。实际上, 基于二维TMDCs的诸多应用里, 大部分器件都可以在柔性基底上实现。因此, 二维TMDCs在可穿戴的柔性设备上具有不可替代

的重要作用。可以预期在不远的未来, 这类新型器件一定会突破传统硅基器件的限制, 在全新的应用领域大放异彩。

5 总结和展望

二维TMDCs的化学组分和晶体结构多样性决定了其丰富的物理化学性质。更为重要的是, 在实验上可以通过电场、磁场、光场、应力场、温度场以及厚度等多种调控手段对材料的物理性质实施有效的操控。因此, 二维TMDCs为基础研究与应用开发提供了一个理想的平台。不仅如此, 随着样品生长技术的不断提高, 许多新型的二维TMDCs材料(包括单相、异质结以及超晶格等结构)被源源不断地发现, 从而带来了诸如二

维磁性、能谷电子学、量子自旋霍尔效应、伊辛超导以及非常规超导等众多新奇的物理特性. 而最近发展起来的固相转移技术促进了范德瓦耳斯异质结的研究, 大大丰富了人们的视野. 性质迥异的TMDCs材料堆叠到一起, 可以得到令人惊奇的物理性质. 进一步通过不同的堆叠方式可以制造出自然界原本不存在但性能优异的人工材料. 正是这些充满活力的新方向, 使得二维

TMDCs材料成为当前凝聚态物理研究的热门体系之一.

近年来, 随着量子现象研究的深入, 以及实际应用的迫切需求, 量子计算正受到前所未有的重视^[181]. 由于拓扑量子计算理论上更具有鲁棒性(robust), 因而它是未来量子计算发展的方向^[182,183]. 在目前阶段, 凝聚态物理研究首先需要找到实现拓扑量子计算的合适体系. 因此, 研究者们急切地寻找拓扑超导材料, 希望从

图 11 (网络版彩色)二维过渡金属硫族化合物为寻找拓扑超导提供了理想的实验平台^[58,59,184-189]

Figure 11 (Color online) 2D transition metal dichalcogenides as an ideal platform to search for topological superconductivity^[58,59,184-189]

中找到马约拉纳零能模(Majorana zero mode, MZM); 利用其非阿贝尔的统计特性来实现拓扑量子计算^[182,183]. 目前已经有一些理论与实验上的工作^[58,59,184–189], 开始

尝试利用二维TMDCs寻找拓扑超导, 如图11所示. 可以预见的是, 二维TMDCs一定会在实现拓扑量子计算的道路上发挥至关重要的作用.

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Summary for “二维过渡金属硫族化合物的研究进展”

Recent progress in two-dimensional transition metal dichalcogenides

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Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been emerged as a new class of van der Waals materials since the successful isolation of graphene. The strong spin-orbit coupling (SOC) and two-dimensionality give rise to plenty of novel physics including metal-insulator transition, charge density wave (CDW), valleytronics, quantum spin Hall effect, and unconventional superconductivity, which make TMDCs an ideal platform to study the fundamental physics and potential applications. In this review, we firstly introduce the crystal structure of 2D TMDCs materials. Then, we summarize the recent progress in the synthesis, novel physical properties, and applications of 2D TMDCs materials. Finally, a summary and an outlook on the topological superconductivity in this field are presented.

2D TMDCs have a chemical formula of MX_2 ($\text{M}=\text{W}, \text{Mo}$ and $\text{X}=\text{Te}, \text{Se}, \text{S}$) with a layered crystal structure. Depending on the coordination environments of M, TMDCs can crystallize in a variety of polytypic structures such as $2H$, $1T$, $1T'$, and T_d phases. In the monolayer $2H$ -TMDCs, the breaking of an in-plane mirror symmetry and the presence of the out-of-plane mirror symmetry lead to an Ising spin-orbit coupling (SOC), which serves as an effective out-of-plane field acting on the copper pair and pins the electron spins to out-of-plane directions. This is called Ising superconductivity, which has been observed in gated MoS_2 , monolayer NbSe_2 and TaS_2 . However, due to the inversion symmetry in monolayer $1T'$ -TMDCs, the introduction of SOC makes them a class of large-gap quantum spin Hall insulators such as monolayer $1T'$ - WTe_2 . Therefore, if we could consecutively tailor the TMDCs' structure from $2H$ to T_d phase, the long-sought topological superconductivity may be realized in one substance by incorporating superconductivity and quantum spin Hall effect together. To explore the extraordinary physics and nanodevice applications, we develop a universal molten-salt-assisted chemical vapor deposition (CVD) method to prepare atomically thin TMDCs, including high-quality 2D superconductors such as monolayer MoTe_2 and NbSe_2 . With the powerful sample growth technique, we demonstrate for the first time that a consecutive structural phase transition from T_d to $1T'$ to $2H$ polytype can be realized by increasing the Se concentration in Se-substituted MoTe_2 . More importantly, the Se-substitution is found to dramatically enhance the superconductivity of the MoTe_2 thin film, which is interpreted as the introduction of two-band superconductivity. Furthermore, in bilayer $1T_d$ - MoTe_2 , we find that the in-plane upper critical field goes beyond the Pauli paramagnetic limit and shows an emergent two-fold symmetry, which is different from the isotropic in-plane upper critical field in $2H$ -TMDCs. We show that this is a result of a new type of asymmetric SOC in $1T_d$ -TMDCs, which has expanded the well-known Ising SOC.

The polytypic structures and strong SOC in 2D TMDCs have led to a variety of novel physics and applications. Recent theoretical works have already shown that 2D TMDCs can be a platform to search for topological superconductivity. With the further development of sample preparation, 2D TMDCs will play an important role in realization of topological quantum computation.

two-dimensional transition metal dichalcogenides, spin-orbit coupling, chemical vapor deposition, structural phase transition, Ising superconductivity

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