Band-Gap Reduction in $(BiCrO_3)m/(BiFeO_3)n$ Superlattices: Designing Low-Band-Gap Ferroelectrics

L. Qiao（School of Physics, University of Electronic Science and Technology of China, Chengdu 610054, China）

[Ques] The study demonstrates that constructing $(BiCrO_3)_m/(BiFeO_3)_n$ superlattices effectively reduces the band gap while maintaining ferroelectric properties, due to interfacial charge reconstruction driven by strain and polarization discontinuity.

[关键问题] 该研究通过构建 $(BiCrO_3)_m/(BiFeO_3)_n$ 超晶格，在保持铁电性的前提下降低带隙，其核心机制是界面处由应变与极化不连续性诱导的电荷重构。

[Sum] The $(BiCrO_3)m/(BiFeO_3)n$ superlattices exhibit significantly reduced band gaps (as low as ~1.6 eV) and maintained ferroelectric polarization, demonstrating superlattice structuring as a viable strategy for designing efficient ferroelectric photovoltaics.

[亮点 1] 超晶格结构实现了显著带隙降低，最低降至约 1.6 eV，不仅低于 BFO 与 BCO 本征值，也低于其合金，成功进入高效光伏吸收区间。

[亮点 2] 尽管带隙降低，体系依然保持高铁电极化（可达 131 μC/cm²）与结构稳定性，展现出兼具光吸收能力与铁电功能的材料优势。

[思考] 该类超晶格在实际制备中对界面质量极为敏感，缺陷、粗糙度及应变松弛是否会破坏其带隙调控效果？此外，除 BFO/BCO 外，是否存在其它铁电/反铁电或磁性组合也能通过超晶格工程实现带隙工程化，实现材料体系的可拓展性？

[拓展阅读 1] 超晶格结构在钙钛矿氧化物中的带隙调控研究

[拓展阅读 1] 超晶格工程是一种适用于多种氧化物体系的能带调控策略，其核心在于界面处的电子重构、应变耦合与极化不连续性。例如在 LaCrO₃/LaFeO₃、BFO/LAO 或 GaN/ZnO 等结构中，也观察到界面电荷重新分布导致的带隙缩窄及局域态形成。这说明"界面工程＋周期调控"是一种通用路线，可系统改变过渡金属

氧化物的轨道占据、电子关联与光吸收行为，特别适用于光伏、光催化和红外探测等跨领域应用。

[拓展阅读 2] 铁电超晶格在光伏器件中的应用潜力与挑战

[拓展阅读 2] 理论表明 BFO/BCO 超晶格兼具合适带隙与强铁电极化，具备铁电光伏的理想特征。但实际器件需解决多项挑战，包括：界面缺陷控制、载流子复合与迁移效率、极化在外界条件下的稳定性、与透明电极的匹配等。此外，铁电光伏常涉及非线性光响应、内建场增强等复杂机制，需借助先进表征与器件模拟进一步评估其真实效率。未来方向包括脉冲激光沉积等高品质生长方法、与二维材料电极耦合，以及在光催化和宽光谱探测中的拓展应用。

[introduction] In the past several decades, researchers have been striving to open different corridors for the production of renewable energy. In this regard, photovoltaics (PVs) have been demonstrated to be a promising renewable energy technology to harvest solar energy [1–3], one of the most abundant energy sources available on Earth [4]. Generally, the performance of PV materials is quantified by the power conversion efficiency (PCE), which can be related to the photovoltage and photocurrent. Recently, building from the initial interest in single-crystal and ceramic materials over four decades ago [5], a rejuvenation of interest in the so-called anomalous photovoltaic effect in noncentrosymmetric thin-film ferroelectrics has driven an urgent search for new materials in this space. Contrary to traditional semiconductor-based PVs, the photovoltage of ferroelectrics is not limited by their band gap, but can be a few orders of magnitude larger than the optical band gap of the material itself [5,6]. In some cases, the photovoltage has been found to be >104 V [2,6]. Generally, the photovoltage is proportional to the magnitude of the electric polarization [6–9]; however, the PCE of ferroelectric materials is normally limited by their small photocurrent density, typically on the order of nA/cm2, which mainly originates from the large intrinsic band gap of these materials (typically 3–4 eV) [2,10]. It is, therefore, of significant importance to lower the band gap of ferroelectric materials without affecting the ferroelectric polarization in an attempt to improve the PCE in PV applications. This is also of great importance for fully characterizing ferroelectric photovoltaic effects, including understanding the performance limits of these devices. While ferroelectric semiconductors do exist [11], for reasons yet
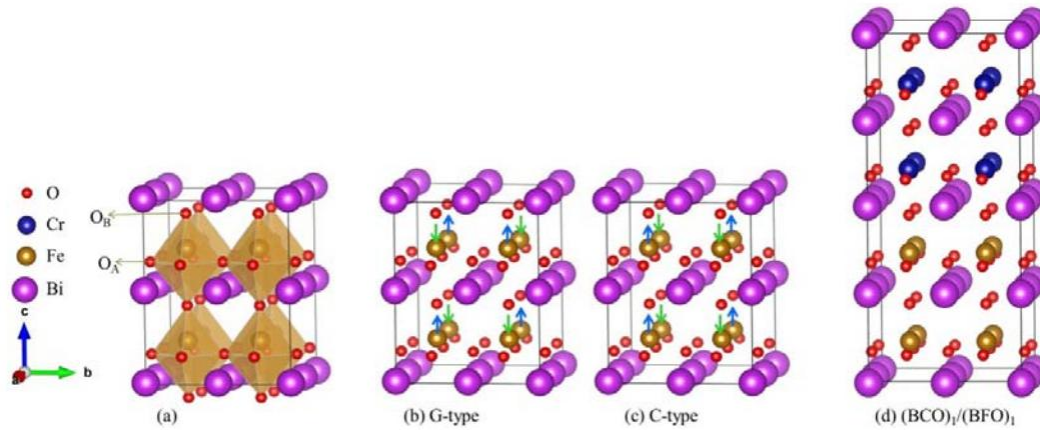
to be understood, the largest effects are observed in oxides, and therefore, finding better oxide materials is a key challenge in the field.

A focus has been in $BiFeO_3$ due to its intrinsic, relatively low band gap (2.67–3.1 eV) [12] and high polarization (90–158 μC/cm2) [13–15]. Importantly, $BiFeO_3$ has been widely investigated for PV applications and so far shows better PCE efficiency than most other ferroelectric materials [2,16–20], making it a highly desirable ingredient in fabricating new ferroelectric photovoltaics. Despite these successes, however, $BiFeO_3$ can only absorb UV light, which constitutes only approximately 20% of the entire solar spectrum, leaving most of the solar energy incident on Earth unexploited [21]. In epitaxial $BiFeO_3$ thin films, there are several possible phases, including structures derived from monoclinic, triclinic, orthorhombic, and tetragonal parent structures. Of particular note is the tetragonal-like phase, which is actually a slightly monoclinically-distorted tetragonal structure, and has a large c/a lattice parameter ratio of approximately 1.26 and a giant spontaneous polarization approaching approximately 150 μC/cm2. With this in mind, it is meaningful to reduce the band gap of tetragonal-like $BiFeO_3$, while maintaining the large spontaneous polarization, to enhance the PCE. On the other hand, $BiCrO_3$ is another ferroelectric material, also with an active lone pair on the bismuth cation [22], which is often used to tune the band gap and photocurrent of $BiFeO_3$ [23–26], e.g., through alloying. We have recently studied alloyed $BiCrO_3$- $BiFeO_3$ films and found that chromium substitution can help to reduce the band gap by approximately 0.8 eV for solid solution films and improves charge transport [27]. The $BiCrO_3/BiFeO_3$ bilayer films, synthesized using a sol-gel technique, were found to exhibit a band gap of approximately 2.25 eV (smaller than the value of 2.64 eV of $BiFeO_3$) and a short circuit photocurrent density of 0.08 mA/cm2 (higher than the value of 0.007 mA/cm2 for a single-layer $BiFeO_3$ film) [28]. Multiferroic $BiFeO_3/BiCrO_3$ heterostructures have also been studied experimentally [10], and it was reported that the photocurrent density and photovoltage can be tuned by the thickness and the number of $BiFeO_3/BiCrO_3$ bilayers and that the highest photocurrent density value (approximately 0.013 mA/cm2) was recorded in 60-nm-thick heterostructures (including two $BiFeO_3/BiCrO_3$ bilayers with each layer of a thickness of 15 nm).

More recently, significant band-gap reduction has been realized in double-perovskite Bi2CrFeO6, in which *B*-site-cation ordering controlled by film synthesis results in a remarkable PCE of over 8.1% under air mass (AM) 1.5 G irradiation [21]; a new record for inorganic perovskites in conventional solar-cell applications. The mechanism of enhanced visible-light absorption and its correlation with cation ordering in the double-perovskite Bi2CrFeO6, however, is not clear. It is well known that for perovskites, achieving *B*-site-cation ordering is very difficult (and it is particularly sensitive to oxygen partial pressure and growth temperature) as the thermodynamic window allowing for the realization of such ordered states is extremely narrow. This has been shown true in a number of systems, including La2VMnO6 [29], La2CrFeO6 [30], La2NiMnO6 [31], etc. On the other hand, superlattice ordering is also a powerful method to engineer ordered double-perovskite structures. For example, long-range ferromagnetism has been reported in LaCrO3/LaFeO3 superlattices, which is unexpected, given that both LaCrO3 and LaFeO3 are antiferromagnetic [32–34]. Therefore, by creating an atomically-ordered state via superlattice structuring of the aforementioned BiFeO3 and BiCrO3, one might expect to yield interesting electronic structure and material properties, distinct from alloys. There are limited studies on BiCrO3/BiFeO3 super lattices, and those which do exist are focused mainly on traditional ferroelectric behavior. For example, using a scanning nonlinear dielectric microscope, researchers found that the polarization in such supelattices is reversible and thus suggested that the super lattices are ferroelectric at room temperature [35]. The ground state properties of BiFeO3/BiCrO3 super lattices, such as the electronic structure, intrinsic band gap, and ferroelectric polarization, are, however, not well developed.

Here, we report a density functional theory (DFT) investigation of the lattice geometrical and electronic properties of (BiCrO3) /(BiFeO3) super lattices. Systematic study shows that the band gap of the super lattices is widely tunable, and can take values well below those of either component by itself, while still maintaining the ferroelectric polarization. Unexpectedly, the optimized band gap of approximately 1.6 eV for the BiCrO3/BiFeO3 super lattice is not only smaller than both the single-layer BiFeO3 and BiCrO3, but is also smaller than the equivalent Bi_{f0}(Fe,Cr)O3 alloy [27]. This surprising result is the consequence of charge reconstruction due to lattice strain, octahedral distortion, and polarization discontinuity at the superlattice interfaces. We also show that the

ferroelectric and magnetic properties of the superlattice are not strongly affected. These results demonstrate that superlattice structuring can be an effective strategy for the design of low band gap oxide semiconductors with fundamental band gaps much smaller than that of either parent material, thus opening new perspectives for ferroelectric PVs.

(a) (b) G-type (c) C-type (d) $(BCO)_1/(BFO)_1$

Enhanced Voltage-Controlled Magnetic Anisotropy and Field-Free Magnetization Switching Achieved with High Work Function and Opposite Spin Hall Angles in W/Pt/W SOT Tri-Layers

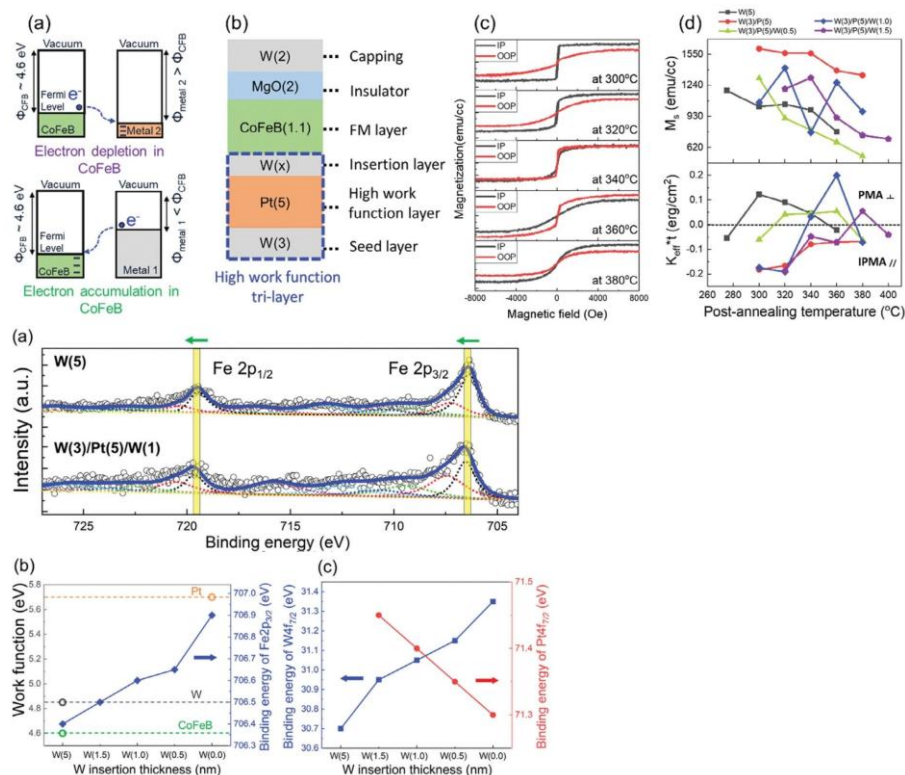（利用 **W/Pt/W** 自旋轨道矩三层结构的高功函数与相反自旋霍尔角实现增强型电压控制磁各向异性及无场磁化翻转）

Yu-Chia Chen、Qi Jia、Yifei Yang、Yu-Han Huang、Deyuan Lyu、Thomas J. Peterson、Jian-Ping Wang*

[Ques] 传统电压控制磁各向异性（VCMA）方法在 CoFeB/MgO 界面的系数较低，本文是如何提升 VCMA 效应的？

[Ques] 一般来说，SOT 器件需借助外部磁场打破对称性才能实现磁化翻转，本文是如何实现无外部磁场磁化翻转的？

日期：2025-11-25

[关键问题] 通过高功函数诱导的电子耗尽增强 VCMA，并通过相反自旋霍尔角在三层结构内产生对称性破缺，实现无需外磁场的 SOT 磁化翻转。

[Sum] 本文通过设计 W(3 nm)/Pt(5 nm)/W(x nm)复合重金属三层 SOT 底提升 VCMA 效应：利用 Pt 的高功函数（5.7 eV，高于 CoFeB 的 4.6 eV）和强电负性，在热平衡状态下诱导 CoFeB/MgO 界面发生电子耗尽（经 XPS 和 UPS 验证，Fe 2p 轨道结合能提升≈0.25 eV，电子密度降低）；通过调控 W 插入层厚度（最优为 1 nm）优化电子耗尽程度，最终使 VCMA 系数超过 100 fJ·V⁻¹·m⁻¹，较纯 W 底层提升十倍，且正负电场下分别达到−99.5 和−12.2 fJ·V⁻¹·m⁻¹。

[Sum] 本文通过整合相反自旋霍尔角产生竞争自旋电流**实现无外部磁场磁化翻转：W 与 Pt 具有相反的自旋霍尔角，在三层结构中形成竞争自旋电流，进而生成垂直有效场以打破铁磁层对称性；当 W 插入层厚度为 1 nm 时，阻尼类（DL）和场类（FL）力矩均接近零（ζ_DL≈−0.003±0.001，ζ_FL≈−0.001±0.03），无需外部磁场即可实现确定性 SOT 翻转，翻转电流约±7.5 MA·cm⁻²，1 ms 脉冲宽度下翻转概率达 92.5%。

[亮点 1] 通过引入高功函数 Pt 并优化 W 插入层厚度，成功在 CoFeB/MgO 界面诱导强电子耗尽，使 VCMA 系数提升至百 fJ·V⁻¹·m⁻¹量级，为降低 SOT-MRAM 写入能耗提供突破性方案。

[亮点 2] 利用 W 与 Pt 的相反自旋霍尔角构建竞争自旋电流，实现无需外部磁场的确定性 SOT 翻转，为无场 VGSOT 器件提供可大规模集成的材料与结构设计思路。

[思考] 本文通过电子耗尽提升 VCMA，但电子态调控仍依赖界面电荷。未来可探索利用二维材料界面、氧化物极化或界面电荷俘获机制，实现更灵活且更强的界面电荷工程，以进一步放大 VCMA 效果。

[思考] 竞争自旋电流的无场翻转证明了"角度工程"的可行性。未来可结合拓扑材料、里德伯态磁性材料或 Rashba 界面，构建可自动产生偏置场的自旋结构，实现更低电流、稳定性更高的零场 SOT 器件。

[拓展阅读 1]（针对主编问题：W 插入层厚度控制及回跳效应的稳定性）

日期：2025-11-25

[拓展阅读 1] W/Pt/W 结构中 W 插入层的最优厚度仅约 1 nm，这意味着原子级波动就可能显著影响电子耗尽程度及自旋电流分布。在工业量产中，常采用高均匀度磁控溅射结合闭环反馈的厚度控制系统（如晶振监控、反射率监控）来保证亚纳米级的层厚一致性。此外，可通过在界面加入自对齐层或采用高表面迁移率材料平滑底层，进一步减少局部粗糙度导致的性能漂移。

[拓展阅读 1] 关于无场翻转中的"回跳效应"，其本质是电流脉冲导致局部焦耳热增强热涨落，使磁化暂时偏离稳定态。若器件尺寸缩小，该效应可能更明显，从而影响 MRAM 的写入确定性。可通过提高热稳定因子（增厚自由层、使用合金提高垂直各向异性）、采用更短脉冲宽度或引入热沉层来减轻回跳。也可利用脉冲形状优化，如脉冲衰减或预偏置脉冲，降低写入后的热扰动，使器件长期稳定性得到保障。

[拓展阅读 2]（针对主编问题：工艺兼容性与正负 VCMA 的不对称性）

[拓展阅读 2] 与 Ta/Pd/Ta 等结构相比，本研究的 W/Pt/W 结构在工业兼容性方面具有明显优势。W 与 Pt 均可通过常规直流或射频磁控溅射稳定沉积，并与现有 MRAM BEOL 工艺兼容；同时 Pt 具备较好化学稳定性，有助于提高界面重复性与可靠性。成本方面，Pt 虽价格较高，但其功能性（高功函数、高自旋轨道耦合）可减少层数与后续退火步骤，使整体工艺复杂度降低。

[拓展阅读 2] 关于 VCMA 系数在正负电场下的强烈不对称性（−99.5 vs −12.2 fJ·V^{-1}·m^{-1}），其原因在于电子耗尽主要发生在正向电场下，而反向电场难以同等程度地恢复电子态分布。这意味着在实际器件中应优先采用单极性、正向电场为主的写入脉冲，以最大化调控效率。负向电场脉冲可作为辅助调节，但在能耗和速度上不具优势。因此，在器件设计上需要发展"单极性写入策略"，并优化栅极材料以提升双极性响应，使电压控制具备更高灵活性。

[introduction] Spintronic-based memory is a promising candidate for beyond-CMOS technology by leveraging the intrinsic spins of electrons alongside their charges, enabling faster and more power-efficient devices.[1-4] One notable technology in the spintronic-based memory realm is Spin-Transfer Torque (STT)-MRAM. STT-MRAM manipulates magnetic moments using a spin-polarized current instead of an external magnetic field, overcoming scaling limitations.[5-7] When a spin-polarized current flows through a ferromagnetic layer, it exerts a torque on the magnetic moments within the material.[8-10] However, reliability issues stemming from high-current stress on the interface have

prompted research into SOT-MRAM, which originates from the spin Hall effect in heavy metals.[11, 12]
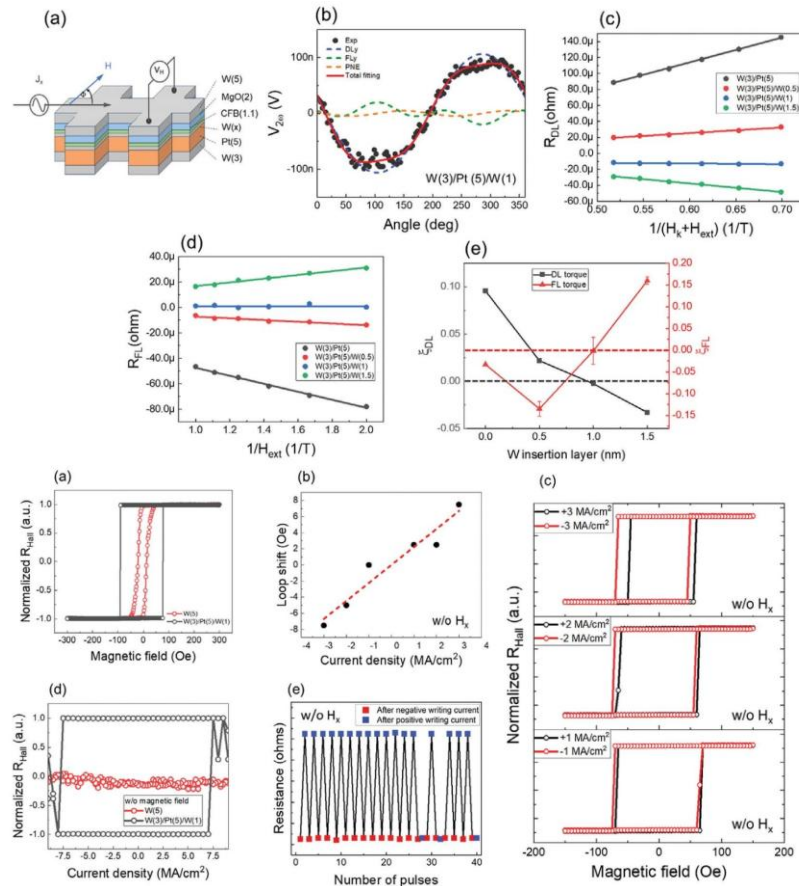
SOT arises from spin accumulation at the interface between ferromagnetic and heavy metal layers, with spin current generation attributed to spin-orbit coupling (SOC) such as the spin Hall effect and the Rashba–Edelstein effect.[13-15] However, the torque generated solely by the SOT effective field is insufficient for flipping PMA magnetization and requires an external magnetic field. Therefore, various solutions have been proposed to break the symmetry and achieve field-free SOT switching, such as generating an in-plane internal effective field through antiferromagnetic interlayer exchange bias or interlayer exchange coupling, lateral structural asymmetry, low symmetry materials, opposite spin Hall angles materials, spin current gradient, lateral spin-orbit torques, and chiral magnetic domain wall.[16-27]
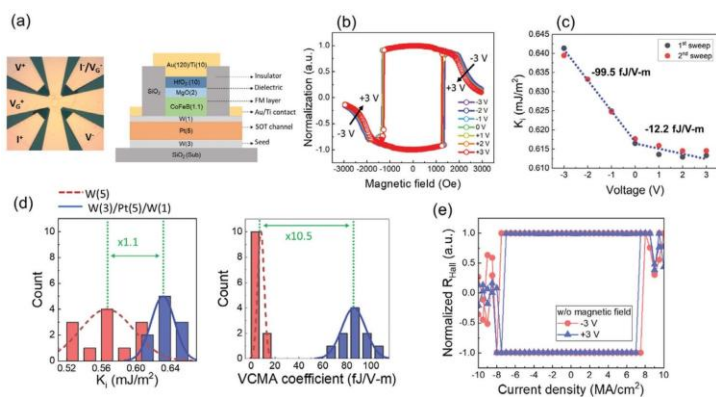
VCMA is a promising strategy to assist STT and SOT-MRAM in lowering energy consumption.[28, 29] It operates by dynamically adjusting the energy barrier height at the interface between an insulator and a ferromagnetic layer using an external voltage bias through the intricate interplay between the electronic states of the ferromagnetic materials and the tunnel barrier.[30-32] Specifically, the dynamics of electron occupancy in the 3d orbitals of the ferromagnetic materials and the 2p orbitals of the tunnel barrier are crucial in shaping the magnetic anisotropy.[33, 34] However, this traditional VCMA approach is inefficient for supporting STT-MRAM and SOT-MRAM, which requires a VCMA coefficient >1000 and >300 fJ V^{-1}m^{-1}, respectively.[29]

In pursuit of enhancing VCMA, Zhang et al. theoretically proposed a bidirectional VCMA effect up to 1.1 pJ V^{-1}m^{-1} in heavily electron-depleted Fe/MgO interfaces.[34] In a related study, Peterson et al. explored electron depletion levels in CoFeB by proposing and implementing a tri-layer underlayer material (Ta/Pd/Ta) with a tunable work function.[35] This approach effectively shifted the chemical potential at the CoFeB/MgO interface, leading to an enhanced VCMA response through the electron depletion mechanism, as validated by DFT calculations. The observed trend in VCMA suggested that the achieved electron depletion was insufficient, necessitating further exploration of underlayers with even higher work functions.\

In this study, we explore a novel design strategy that incorporates high work function and high-electronegativity metals to induce VCMA through electron depletion at the PMA

CoFeB/MgO interface and leverages opposite spin Hall angles in a tri-layer SOT channel to generate competing spin currents. Our investigation focuses on the W(3 nm)/Pt(5 nm)/W(x nm) underlayers in the CoFeB/MgO system. The electron depletion behavior at the CoFeB/MgO interface was confirmed using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Notably, the high work function of Pt in W(3 nm)/Pt(5 nm)/W(x nm) underlayer (W/Pt ∼ 4.8/5.7 eV) plays a crucial role in enhancing the VCMA effect, showing an improvement of approximately ten times greater compared to a pure W underlayer. Besides, field-free magnetization switching was achieved in the W/Pt/W tri-layer by generating a perpendicular effective field through opposite spin Hall angles.

日期：2025-11-25

(a) ... Au(120)/Ti(10) ... HfO₂ (10) ... SiO₂ ... MgO(2) ... CoFeB(1.1) ... W(1) ... Au/Ti contact ... Pt(5) ... W(3) ... SiO₂(Sub) ... Insulator / Dielectric / FM layer / SOT channel / Seed

(b) Normalization (a.u.) vs Magnetic field (Oe) — -3 V, +3 V

(c) K_i (mJ/m²) vs Voltage (V) — 1st sweep, 2nd sweep; -99.5 fJ/V-m; -12.2 fJ/V-m

(d) W(5); W(3)/Pt(5)/W(1); Count vs K_i (mJ/m²) ×1.1; Count vs VCMA coefficient (fJ/V-m) ×10.5

(e) Normalized R_{Hall} (a.u.) vs Current density (MA/cm²) — w/o magnetic field, -3 V, +3 V

SPELLs BeyondStory 编辑部

编辑：闫婷

投稿人：杨铸，梁宏铭

日期：2025-11-25