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傾斜磁異向性在鉑/鈷/鉑異直結構中對自旋軌道矩無場翻轉的
影響

The Effect of Tilted Magnetic Anisotropy on Field-Free Spin-
Orbit Torque Switching in Pt/Co/Pt Heterostructures

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本論文係 **林孟頡** (R11527078) 在國立臺灣大學材料科學與工程學系、所完成之碩士學位論文，於民國 113年7月29日 承下列考試委員審查通過及口試及格，特此證明。

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摘要



隨著物聯網(IOT)設備與高性能計算(HPC)的需求增加，使得磁性記憶體逐漸受到重視。由於電流注入的幾何結構差異，相較於現今量產主流的自旋轉移矩記憶體(STT-MRAM)，自旋軌道矩記憶體(SOT-MRAM)擁有更高的開關速度以及耐用性，但是要實際應用於元件中，我們需要提供外加磁場來打破對稱性以實現磁性的確定性的磁性切換。目前有一種無場翻轉方案是透過在濺鍍過程中將重金屬層斜向生長，以傾斜垂直磁異向性(tilted PMA)。我進一步測試了在鈹/鉑/鈷/鉑/鈹(Ta/Pt/Co/Pt/Ta)不同層之間的斜向生長對於無場翻轉的影響，並且發現了組合不同的斜向生長層可以進一步提高無場翻轉比率並降低翻轉的電流。再經由不同角度的磁滯曲線偏移，可以驗證是由傾斜磁垂直異向性導致的。隨後也探討了退火對於斜向生長鉑晶格結構與無場翻轉的影響，發現退火帶來的原子重新排列與混合會破壞傾斜磁異向性的形成，如何在退火後保留傾斜磁異向性甚至透過退火增強會是一個具有發展潛力的課題。

關鍵字：自旋軌道矩、自旋霍爾效應、無場翻轉、傾斜磁異向性、磁性材料、磁性記憶體

Abstract



With the increasing demand for Internet of Things (IoT) devices and high-performance computing (HPC), magnetic memory is gaining attention. Due to the differences in the geometry of current injection, Spin Orbit Torque Magnetic Random Access Memory (SOT-MRAM) offers higher switching speeds and durability compared to the mainstream Spin Transfer Torque MRAM (STT-MRAM) currently in mass production. However, for practical application in devices, an external magnetic field is required to break symmetry for deterministic magnetic switching. Currently, a field-free switching scheme involves the oblique growth of the heavy metal layer during sputtering to tilt the perpendicular magnetic anisotropy (tilted PMA). I further tested the effects of oblique growth between different layers of tantalum /platinum /cobalt /platinum /tantalum on field-free switching and found that combining different obliquely grown layers can further improve the field-free switching ratio and reduce the switching current. Shifts in the hysteresis curves at different angles verify that this is caused by the tilted perpendicular magnetic anisotropy. Subsequently, the effects of annealing on the lattice structure of obliquely grown Pt and field-free switching were also investigated. It was found that the atomic rearrangement and mixing caused by annealing disrupt the formation of tilted magnetic anisotropy. How to retain the tilted magnetic anisotropy after annealing, or even enhance it through annealing, will be a promising topic for further development.

Keywords: Spin Orbit Torque, Spin Hall Effect, Field-Free Switching, Tilted Magnetic

Anisotropy, Magnetic Materials, Magnetic Memory

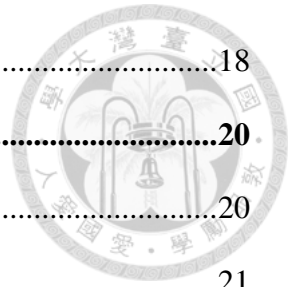


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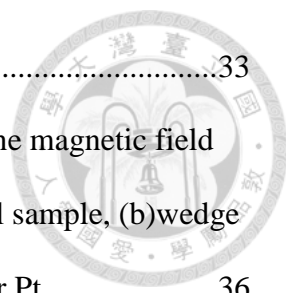


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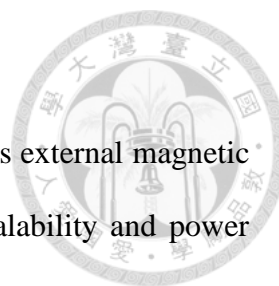
Chapter 1 Introduction

1.1 Magnetoresistive Random Access Memory

Magnetoresistive Random Access Memory (MRAM) is a type of non-volatile memory technology that uses magnetic states to store data. Unlike traditional memory technologies (DRAM and SRAM) which require power to maintain the stored information, MRAM retains data even when the power is off, making it a persistent memory. This provides a significant advantage in applications where data persistence is crucial, such as in embedded systems, automotive electronics, and wearables.

The mechanism of MRAM is that resistance of a material changes in response to a magnetic field. This effect is utilized to detect and manipulate the magnetic orientation of the ferromagnetic layers within the MRAM device.

In MRAM, data is stored in magnetic cells. Each cell consists of a magnetic tunnel junction (MTJ), which is composed of two ferromagnetic layers separated by a thin insulating layer (often made of MgO). One of the ferromagnetic layers is magnetically fixed, or pinned, while the orientation of the other layer (the free layer) can be manipulated to represent data (0s and 1s). The read operation in MRAM is performed by measuring the resistance of the MTJ. If the magnetic layers are parallel, the resistance is low, indicating a '1'. If they are antiparallel, the resistance is high, indicating a '0'. Writing data in MRAM involves changing the magnetic orientation of the free layer. This can be achieved using magnetic fields, spin-polarized current (Spin Transfer Torque, STT), or Spin Orbit Torque (SOT).



Types of MRAM

Field-Induced MRAM: The earliest form of MRAM, which uses external magnetic fields to write data. This method is less common today due to scalability and power efficiency challenges.

Spin Transfer Torque MRAM (STT-MRAM) uses a spin-polarized current to switch the magnetic orientation of the free layer. STT-MRAM offers better scalability and lower power consumption than field-induced one, making it suitable for broader applications.

Spin Orbit Torque MRAM (SOT-MRAM) is the newest technology that uses spin-orbit coupling to switch the magnetic state. SOT-MRAM potentially offers faster switching speeds and lower power consumption than STT-MRAM.

MRAM is considered a promising technology for various applications, including enterprise storage, in memory computing (Fig.1.1b), AI, and any other application requiring quick, persistent storage.

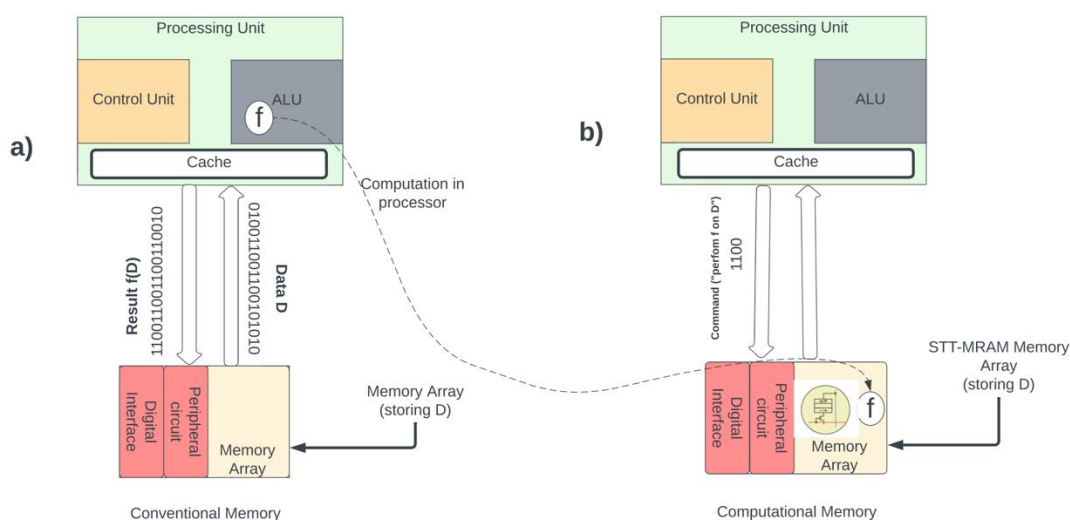


Figure 1. 1: (a) Typical von Neumann architecture and (b) in-memory computing architecture. F indicates function. [9]



1.2 Magnetism

1.2.1 Paramagnetism

When certain materials which are weakly attracted by an external magnetic field and form internal induced magnetic fields in the direction of the applied field (Fig.1.2). This effect is unlike ferromagnetism where permanent magnets are created, they do not retain magnetization when external magnetic field is removed because of the thermal motion disarranges the spin orientations.

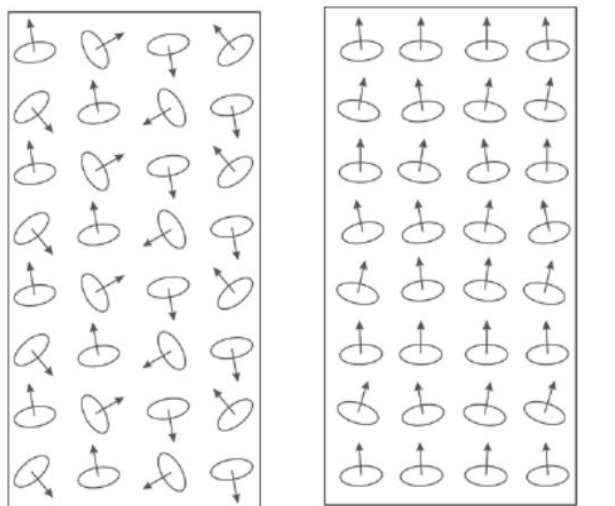


Figure 1. 2: Illustration of paramagnetism. [2]

When the temperature is even higher, the thermal motion makes the atom more disorder. The alignment of the magnetic moment was randomized under phase transformation so that ferromagnetic and ferrimagnetic will turn into paramagnetic. This is called the Curie temperature T_C [3]. The magnetic susceptibility χ above T_C is given by Curie-Weiss Law [5] :

$$\chi = \frac{C}{T - T_C} \text{ or } M = C \frac{H}{T - T_C} \quad (1.1)$$



where C represents the Curie constant.

1.2.2 Diamagnetism

When a magnetic field is applied on certain material, it induces a magnetic field in an opposite direction of the applied field, generates a repulsive force, the phenomenon is called diamagnetism. This can be considered as Lenz's Law: There are two electron orbits, one moving clockwise and the other counterclockwise. When an external magnetic field is applied in the direction entering the page, it increases the centripetal force for the clockwise-moving electron, thereby increasing its magnetic moment directed out of the page, and vice versa. The net effect will be repulsive and the magnetic susceptibility χ will be negative. All materials have diamagnetism even for the ferromagnetic and paramagnetic ones, but it is weak to be overcome by other magnetic effects.

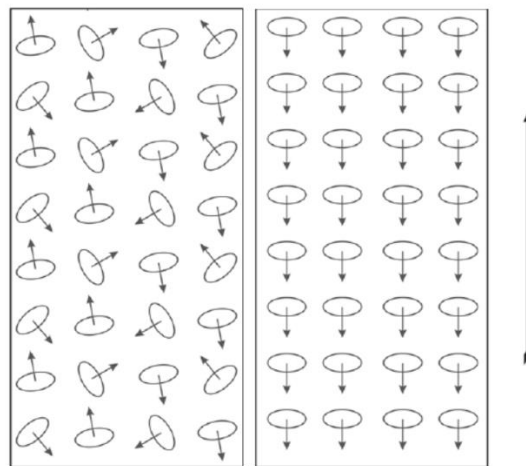


Figure 1. 3: Illustration of diamagnetism [2]

1.2.3 Ferromagnetism

In ferromagnetic materials there are many unpaired electrons. Due to exchange interactions [1], the spins of these electrons tend to align in the same direction as adjacent unpaired electrons. There are many magnetic domains and within each domain all

electron spins are aligned in one direction, creating a "saturated magnetic moment". Since the direction and magnitude of magnetic moments differ between domains, the net magnetic moment and magnetization vector of an unmagnetized ferromagnetic material is almost zero. When an external magnetic field is applied, the magnetic moments of these domains tend to align with the direction of the external field, forming a strong magnetization vector and its induced field (Fig.1.4).

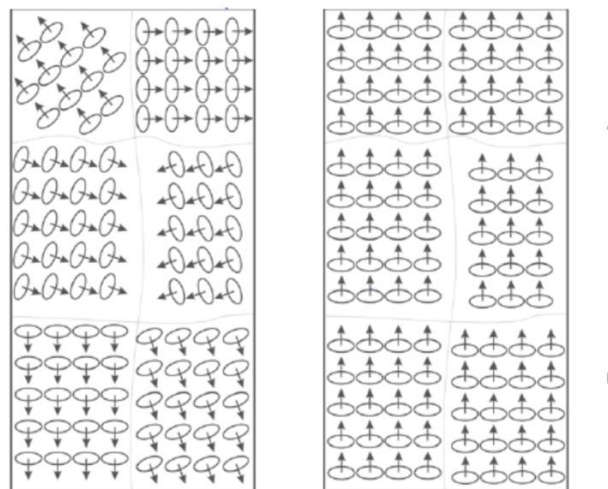


Figure 1. 4: Before and after magnetic field applied on a ferromagnetic material.[2]

As the external field increases, the magnetization intensity also increases, until it reaches the "saturation point" where the net magnetic moment equals the saturated magnetic moment. At this point, further increasing the external magnetic field will not change the magnetization intensity. If the external magnetic field is reduced, the magnetization intensity will also decrease, but it will not match the previous magnetization intensity for the same external magnetic field. The curve of magnetization intensity versus external magnetic field forms a hysteresis loop (Fig .1.5). Consider exchange interaction and must have unfilled electron shells, only Fe, Co and Ni are ferromagnet in room temperature.

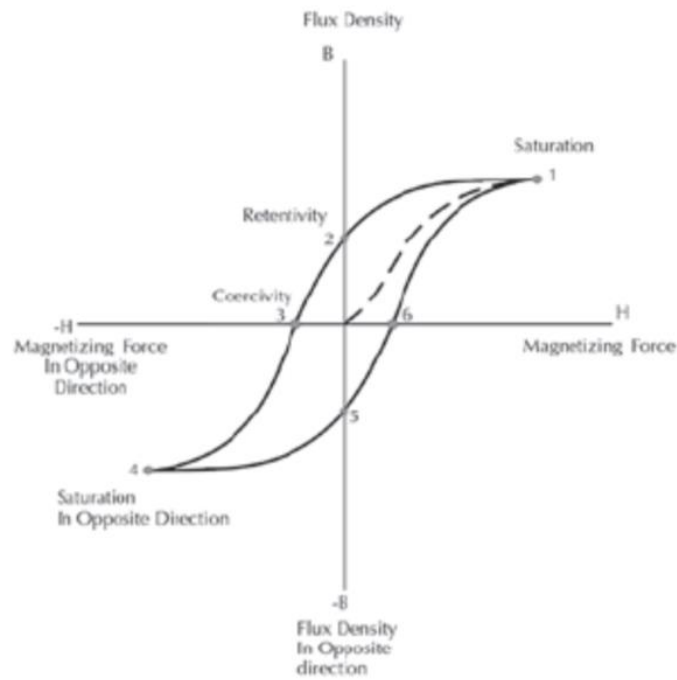


Figure 1. 5: Hysteresis loop of magnetization. [2]

1.2.4 Antiferromagnetism

Louis Néel discovered antiferromagnetic material at the 1930s. Due to exchange coupling, the magnetic moment tends to align. However, unlike ferromagnetic, the moments align in an antiparallel way meaning that the spin orientation of neighboring electron is opposite (Fig.1.6a), making both the total magnetization and magnetic susceptibility χ close to zero. By specific material design, non-collinear antiferromagnet (Fig 1.6b) can be realized with non-parallel moment orientation but zero total magnetization [6].

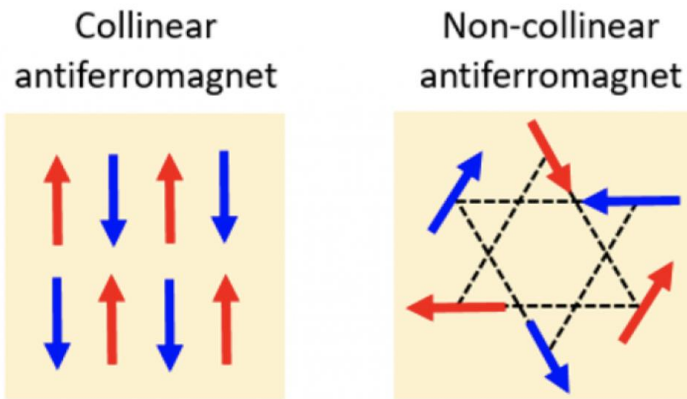


Figure 1. 6: Collinear and non-collinear antiferromagnet [6]

As the temperature reaches 0k, the direction of neighboring magnetic moments should perfectly reverse making the magnetic susceptibility zero. In the other hand, when the temperature is over the Néel temperature T_N , the thermal motion will break the long-range order of antiferromagnet and become paramagnetic [7] (Fig.1.7). Antiferromagnetic follows the Curie-Weiss Law (1.1) with negative Curie constant, which cause by the negative exchange interaction between neighboring electrons [4].

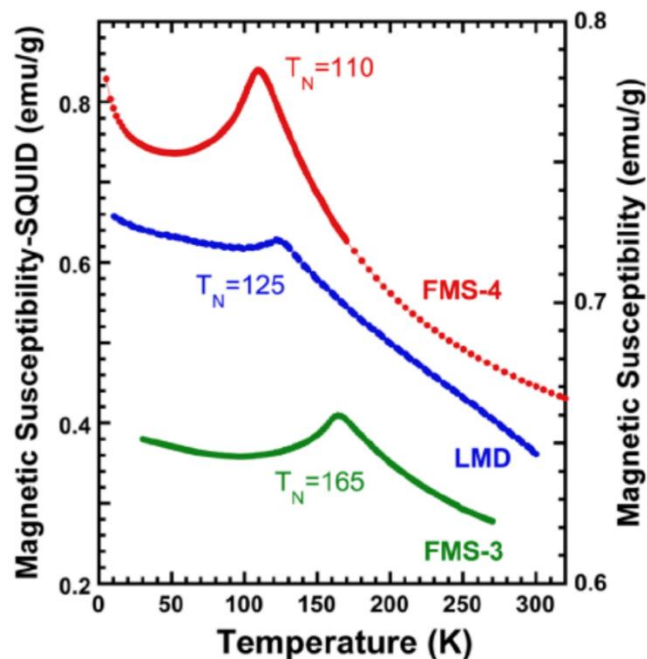


Figure 1. 7: Magnetic susceptibility by temperature to determine T_N of ferromanganese alloys. [7]



1.3 Hall effect

1.3.1 Anomalous Hall effect (AHE)

Late 19th century, American physicist Edwin Herbert Hall discover an effect that is: A cross voltage can be measured when applying a current in FM materials under zero external magnetic field. Since the effect is much different from the original Hall effect, it was later known as anomalous Hall effect (AHE) [8].

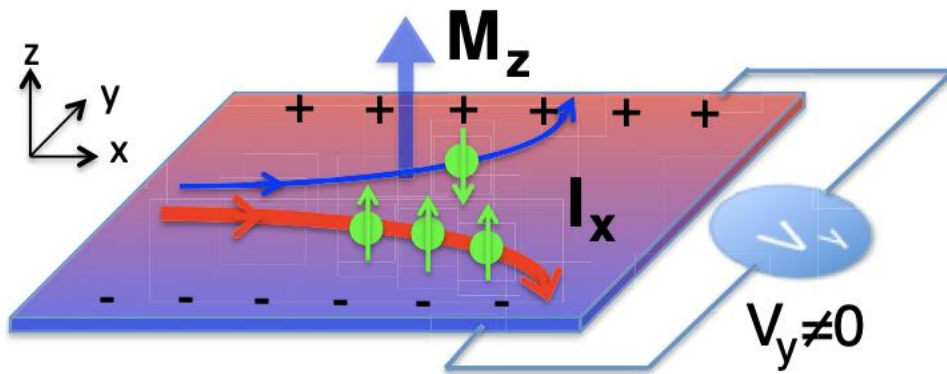


Figure 1. 8: Illustration of anomalous Hall effect. [10]

The effect was shown in Fig.1.8. Due to spin orbit coupling (SOC), the electrons that spin in different direction (up or down) will be deflected into separated ways in FM materials. Since the number of electrons with different spin directions varies, a cross voltage can be generated. The resistance R_{xy} can be expressed as

$$R_{xy} = R_O H_z + R_A m_z \quad (1.2)$$

where R_O is the ordinary Hall effect resistance, H_z is the applied field in z direction, R_A is the AHE resistance and m_z is the z-component of magnetization. We can than measure AHE by probing the direction of m_z since R_O is negligible compared to R_A .



1.3.2 Spin Hall effect (SHE)

Spin Hall effect was first predicted by M. I. Dyakonov and V. I. Perel [11], reintroduced by J. E. Hirsch in 1999 [12] and observed by Y. Kato in 2004 [13]. Since the phenomenon is also SOC driven, like the AHE, when a current flows into SHE material, the electrons in different spin direction will deflect into separated ways (Shown in Fig. 1.9).

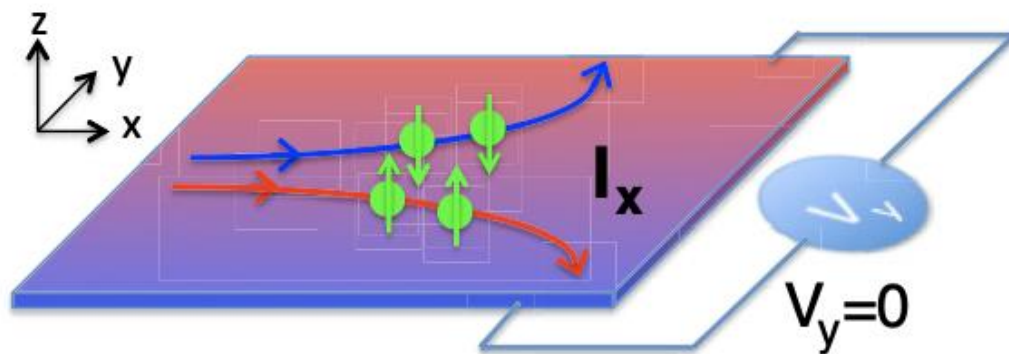


Figure 1. 9: Illustration of spin Hall effect. [10]

Due to the deflection of electrons, a relation between charge current density J_c and generated transverse spin current density J_s can be expressed as

$$J_s = \theta_{SH}(\sigma \times J_c) \quad (1.3)$$

where θ_{SH} represent the spin Hall angle and σ represent the spin polarization. Unlike AHE which is observed in FM materials, SHE was found in nonmagnetic materials and that makes the number of electrons of different spin directions is equal, result in no cross Hall voltage. 5d transition metals (W, Pt, Ta) are promising SHE materials [15][16] because of their strong SOC and good conductivity.



1.3.3 Orbital Hall effect (OHE)

When a current flows through the material, due to the SOC, electrons are deflected because of their distinct spin direction. On the other hand, electrons with different orbital angular momentum (OAM) can also be deflected (Fig. 1.10) even without SOC [17], inducing an orbital current perpendicular to the electric field.

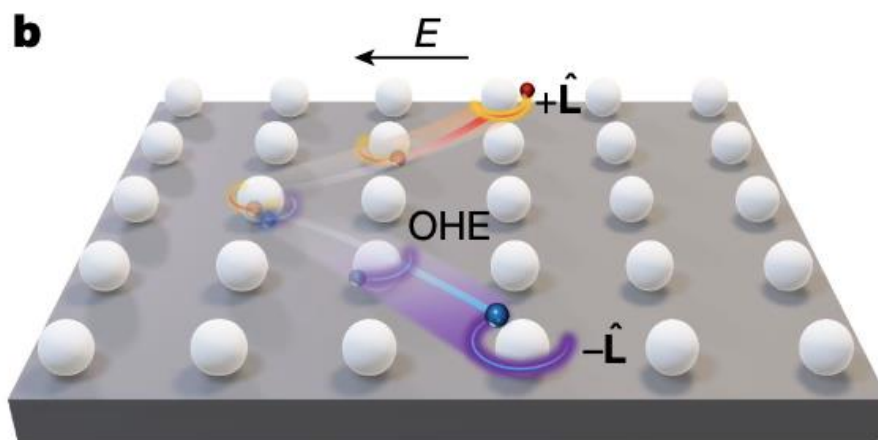
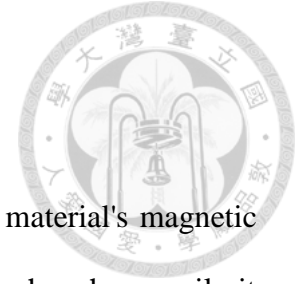


Figure 1. 10: Illustration of orbital Hall effect [17]

OHE has long been theoretically predicted but to observe the direct effect of OHE is challenging since it is hard to separate the contribution from OAM and from spin angular momentum [18]. A group [17] demonstrates a way by using the magneto-optical Kerr effect (MOKE). The MOKE signal confirmed that the OHE-induced moment is larger than the SHE-induced moment. This shows the potential of “orbitronics” and also adding more choices of materials to electrical controlled magnetism since applying the OHE to 3d light transition metals such as Cr [19], Ti [17] and Cu [20] is feasible.



1.4 Magnetic anisotropy

Magnetic anisotropy refers to the directional dependence of a material's magnetic properties. This means that the magnetic behavior of the material, such as how easily it can be magnetized, varies depending on the direction in which an external magnetic field is applied. The easiest direction to magnetize the material is called the easy axis, which is an important factor on the application of magnetic materials.

Magnetic anisotropy was composed of multiple anisotropies in the material including magnetocrystalline anisotropy (MCA), shape anisotropy, strain anisotropy and surface anisotropy. The MCA arises due to the underlying crystal structure of the material. The arrangement of atoms and the spin-orbit interaction within the crystal lattice can make certain directions more favorable for magnetic alignment [21]. Shape anisotropy is caused by demag field which is dependent to the length of the dimension of the object [22]. When applying an external field along the short axis of a thin film, a large demag field will be induced making the magnetization prefer to be in the plane with relatively longer axis. Strain anisotropy changes the preferred magnetization orientation when the material deformed in a dimension that leads to a lattice cell distortion [23]. Surface anisotropy also known as interfacial anisotropy, is induced at the interface of materials. This is origin from the symmetry breaking and may overcome shape anisotropy in some very thin films [24].

1.4.1 In-plane magnetic anisotropy (IMA)

Consider the direction of magnetization easy axis, when the easy axis lies within the x-y plane, an in-plane magnetic anisotropy will be induced. The IMA usually happens on

magnetic single films, because the shape anisotropy is a large component in the total magnetic anisotropy. The effective magnetic anisotropy energy K_{eff} can be express as

$$K_{eff} = K_b + \frac{K_i}{t} - \delta N \frac{M_S^2}{2\mu_0} \quad (1.4)$$

where K_b represents the bulk anisotropy energy (~ 0), K_i is the interfacial anisotropy energy, divided by thickness t , the last term is the shape anisotropy term [24]. As the thickness of FM layer decrease, the effect of shape anisotropy decreases, making K_{eff} increases (Fig. 1. 11). A positive K_{eff} indicates an easy axis that is perpendicular to the x-y plane.

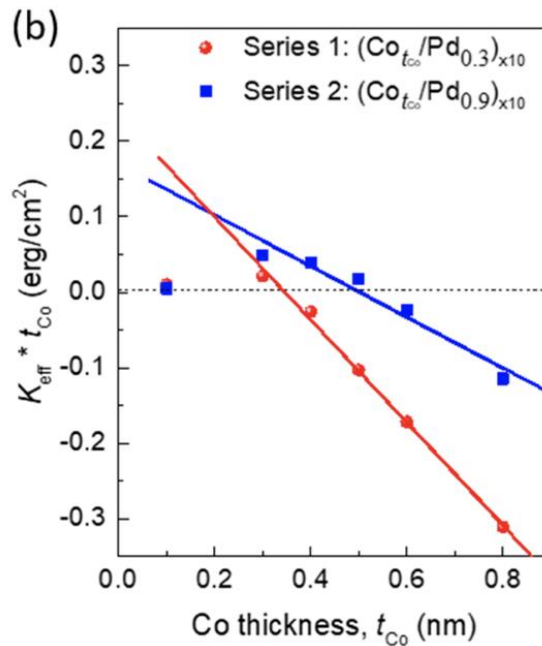


Figure 1. 11: $K_{eff}t_{Co}$ vs Co thickness [25]

1.4.2 Perpendicular magnetic anisotropy (PMA)

Perpendicular magnetic anisotropy (PMA) is the opposite of IMA, which the easy axis stands on the z-direction. The PMA thin film is a much better than IMA ones because

of the enhancement of data storage density so it is widely used in MRAM devices, while IMA was used by recording tapes [26].

PMA have two origins majorly: the bulk and the surface. Some bulk properties like MCA and strain magnetic anisotropy built up the bulk PMA. Report [27] said that comparing to interfacial PMA, bulk PMA materials have larger K and better thermal stability, also, the anisotropy will not be diluted when the film grows thicker. Bulk PMA can be induce in transition metal-rare earth alloys (CoTb, CoGd etc.) [28] [29] and L1₀-ordered alloys [30].

In contrast to bulk PMA, interfacial PMA was induced by the effect that happens when two different elements meet at the interface. Take Pt/Co for example, the interfacial PMA was induced by intermixing of Pt and Co [31], meaning that the two elements are interdiffused or alloyed during the film deposition. Another commonly used interfacial PMA heterostructure is Ta/CoFeB/MgO. In this case, Ta (5d) has strong SOC so the free electrons hybridize with electrons in CoFeB (3d). Also, Ta atoms are directing to MgO (001) crystal orientation forming a strong MCA. Which indicates that the selection of seeding layer is important in PMA films.

In equation 1.4, when calculating the effective magnetic anisotropy energy K_{eff} in a multi-layer structure, after considering the bulk anisotropy term K_b and shape anisotropy term, we will multiply the interfacial anisotropy term K_i by the number of the interface that induces PMA, take CoFeB/MgO for example (Fig 1. 12), interfacial PMA is induced in free layer and MgO, thus for the double (quad) interfaces' structure, K_i is multiplied by 2(4), and so on.

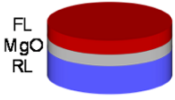
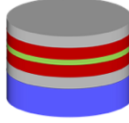
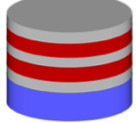
Thermal stability factor $\Delta = E k_B T$ ($E = K_{eff} V$)	Interfacial-anisotropy MTJ		
	Single interface [Ikeda 2010]	Double interfaces [Sato 2012]	Quad interfaces [Nishioka 2019]
Effective magnetic anisotropy energy $K_{eff} = K_b + \frac{K_i}{t} - \delta N \frac{M_s^2}{2\mu_0}$			
Bulk anisotropy energy K_b	~0	~0	~0
Interfacial anisotropy energy K_i	× 1	× 2	× 4
Shape anisotropy energy $-\delta N \frac{M_s^2}{2\mu_0}$	Negative	Negative	Negative

Figure 1. 12: Calculation of K_{eff} in different numbers of interfaces. [24]

1.5 Landau-Lifshitz-Gilbert equation (LLG equation)

The LLG equation was first introduced by Lev Landau and Evgeny Lifshitz in 1935 [33], and later adapted by T. L. Gilbert in 1955 [34]. This differential equation describes the magnetization dynamic in a solid and the relation between magnetization and effective magnetic field. The LLG equation can be expressed as

$$\frac{dM}{dt} = -\gamma^* (M \times H_{eff}) + \frac{\alpha}{M_s} (M \times \frac{dM}{dt}) \quad (1.5)$$

where $\gamma^* = \gamma/(1 + \alpha^2)$, γ represents the absolute gyromagnetic ratio, α is the Gilbert damping constant, H_{eff} is the effective magnetic field (sum of all existing magnetic fields) and M is the magnetization. In an equilibrium system, the magnetization M should be parallel to the effective field H_{eff} , otherwise, the magnetization will undergo precession around the effective field. The motion is described

by the first term called precession term. The second term describes the attenuation of the precession representing the energy dissipation of the system, which is called the damping term.

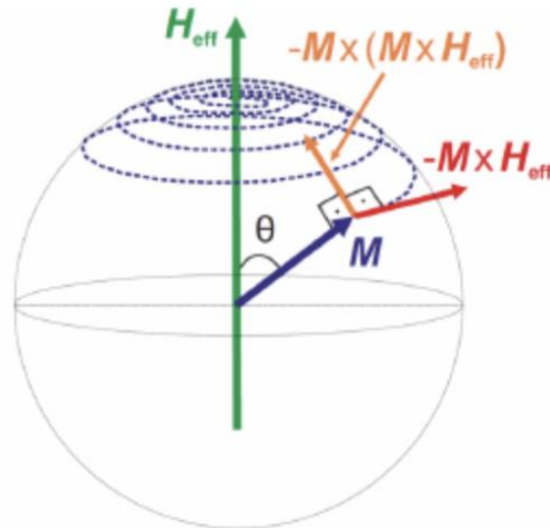
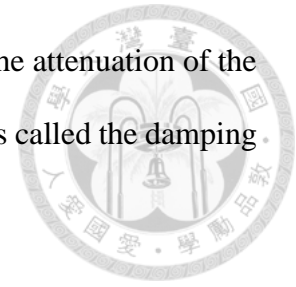


Figure 1. 13: Illustration of the magnetization dynamics under effective field.[35]

1.6 Spin torques

1.6.1 Spin-transfer torque (STT)

J. C. Slonczewski at IBM invented the STT-MRAM in the early 1990s [36]. When the current pass through a FM/NM/FM multilayer, the magnetization of FM layer will be change by the generated STT. By designing the metallic multilayer specifically, the two FM layers can be set in magnetization parallel or antiparallel states. As shown in Fig. 1. 14.

The stability of magnetization for two FM layers is different. The one that its magnetization is easier (harder) to switch is called the free (pinned) layer. When a current flows in the direction from free layer to pinned layer (Fig 1.14a), the electrons will pass pinned layer first and will be spin-polarized by M_{pinned} . After the electrons passing through the NM layer, due to angular momentum conservation, the polarized electrons will give the free layer M_{free} a torque $M_{free} \times (M_{free} \times M_{pinned})$, twisting the magnetization to the same direction as M_{pinned} . This makes two FM layers in a parallel state that has lower resistance. To switching the system to antiparallel, current will then be injected from pinned layer to free layer (Fig 1.14b). The magnetization of free layer M_{free} also polarizes electrons, however, when the polarized electron reaches pinned layer, it is not able to switch M_{pinned} since the material was set to have strong anisotropy. Thus, the electrons will be reflected to free layer with a torque $M_{free} \times (M_{free} \times -M_{pinned})$, switching M_{free} in opposite direction. In the antiparallel state, the resistance of the system is higher.

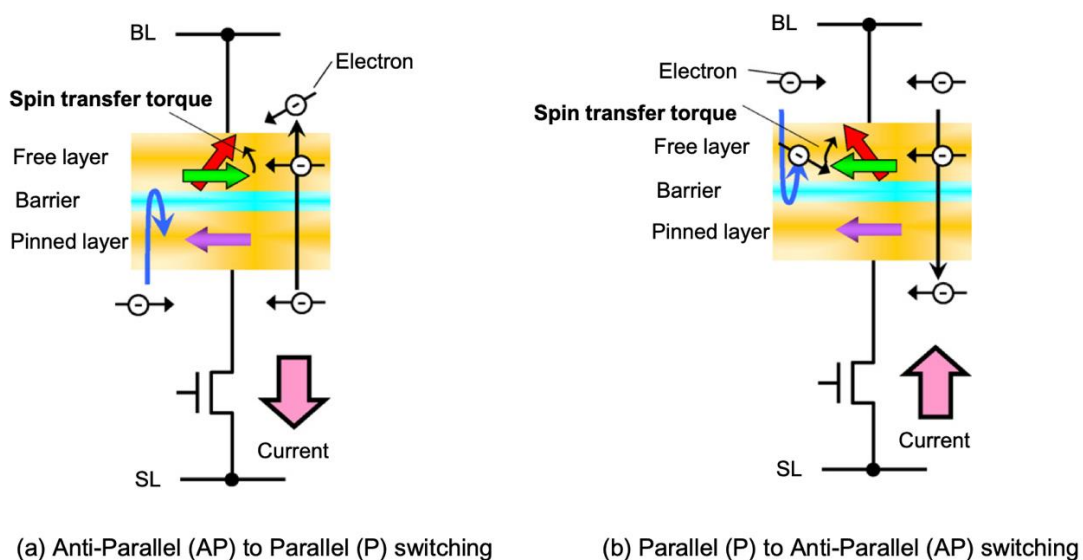


Figure 1. 14: STT-MRAM switching between parallel and antiparallel state. [37]



To calculate the magnetization dynamics in STT-MRAM, a Slonczewski spin transfer torque term is added in LLG equation, the LLGS equation with normalized magnetization m can be expressed as

$$\frac{dm}{dt} = -\gamma(m \times H_{eff}) + \alpha \left(m \times \frac{dm}{dt} \right) + \tau_{DL}(m \times (m \times \sigma)) + \tau_{FL}(m \times \sigma) \quad (1.6)$$

where σ represents the spin polarization, τ_{DL} and τ_{FL} represent damping like STT term and field like STT term, respectively. Since the cross product $m \times \sigma$ decides the direction of τ_{DL} , the angle between m and σ is important. If they are in parallel orientation, τ_{DL} will enhance the damping. On the other hand, the damping abates when they are antiparallel. τ_{FL} compared to τ_{DL} , is relatively small which can be negligible.

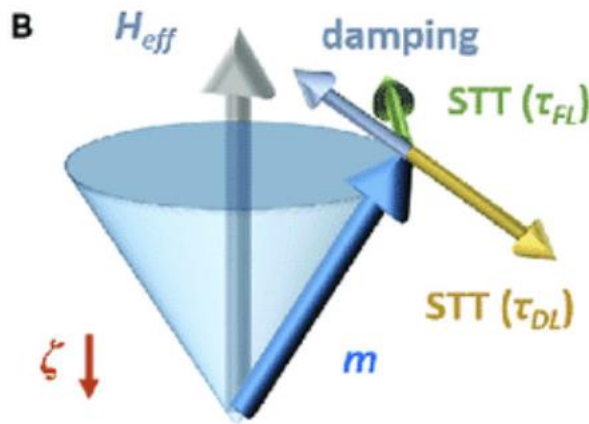
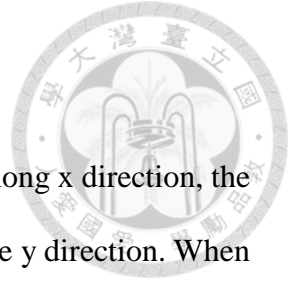


Figure 1. 15: Illustration of field like STT and damping like STT. [38]



1.6.2 Spin-orbit torque (SOT)

As former mentioned, when the current flows in the NM layer along x direction, the SHE induces a transverse spin current with spin polarization along the y direction. When the current flows along z direction, the spins will be injected into the FM layer, exerting a torque on the magnetization of FM, this is called the SOT (Fig 1.16). The spin current J_s corresponded to the input charge current J_c can be described as

$$J_s = \theta_{SH} \frac{\hbar}{2e} J_c \times \sigma \quad (1.7)$$

where θ_{SH} represents the spin Hall angle [39].

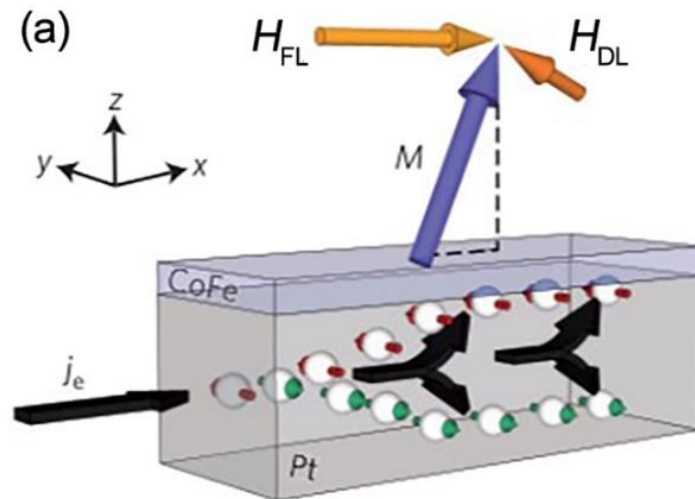


Figure 1. 16: Illustration of SOT in Pt/CoFe bilayer. [39]

Another mechanism of SOT other than SHE is the Rashba effect, which was discovered by Emmanuel Rashba in 1959 [40]. Rashba effect takes place in a system lacking inversion symmetry. The disruption of inversion symmetry can result either from the interface of a bilayer or within the crystal structure. When a charge current is applied, it causes an asymmetric distribution of electrons in k-space (Fig 1. 17), which generates an effective field and induces a nonequilibrium spin density perpendicular to the direction

of the current [39]. This means that if we want to isolate the influence of SHE on SOT, we can design symmetrical structures to minimize the generation of the Rashba effect as much as possible.

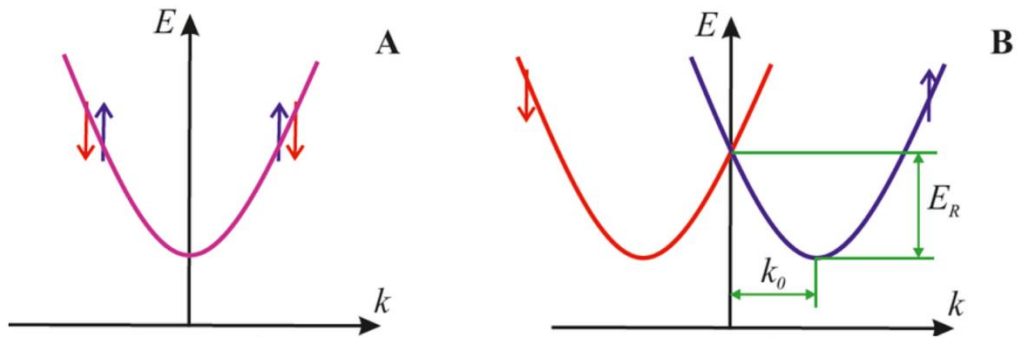
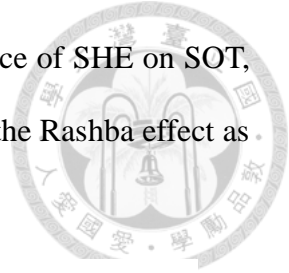


Figure 1.17: Wave function with (A) and without (B) Rashba spin splitting. [41]

The SOT can also be classified into field-like SOT and damping-like SOT, as shown in Figure 1.18. Unlike the STT scenario, the damping-like SOT can only pull the magnetization toward the x direction. To reach deterministic magnetization switching, an external in-plane field is necessary, which is one of the major challenges in manufacturing SOT devices.

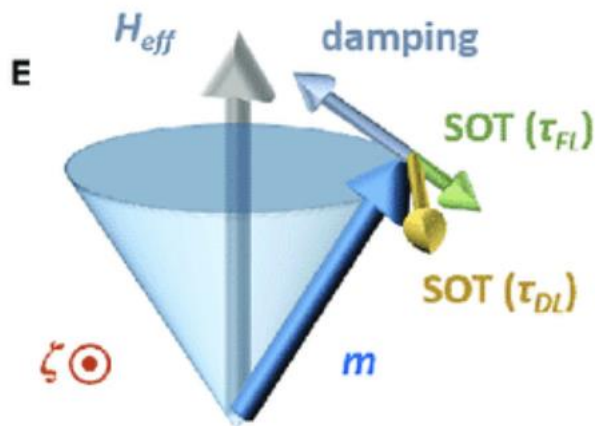


Figure 1.18: Illustration of field like SOT and damping like SOT. [38]



1.7 Field free switching

1.7.1 Idea of field free switching

Consider two states, 1 and 2, where the magnetization of state 1(2) is in $+z(-z)$ direction. To achieve deterministic switching is to switch from state 1 to 2, however, if state 1 is stable, state 2 should be stable as well. Since it is hard to switch from two equally stable state, one of them must be slightly unstable than another one. Therefore, symmetry breaking is necessary to fulfill deterministic switching. By applying a magnetic field toward the $-x$ direction at state 1, deterministic switching can be reach since the applied field have to be in $+x$ direction to remain the symmetry (Fig 1.19). For more practical uses, deterministic switching must happen without the extra field, this is called Field free switching.

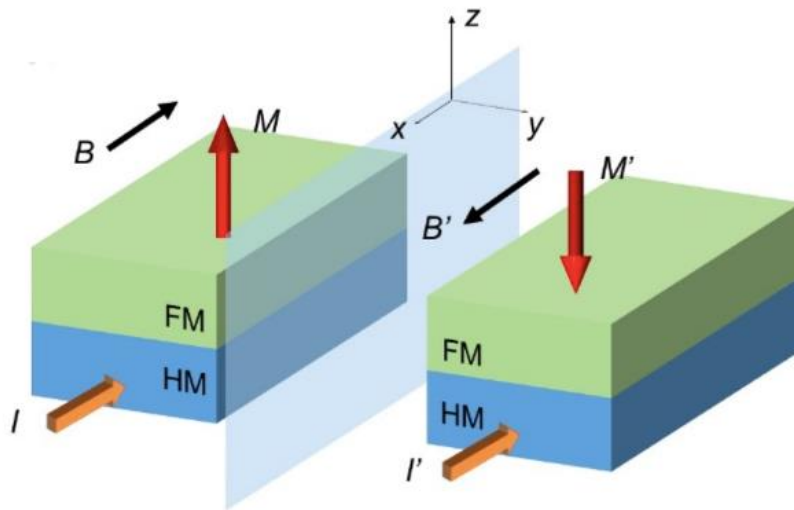
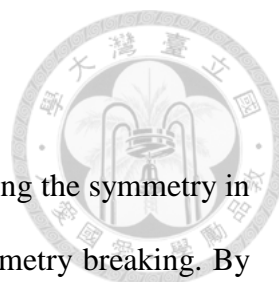


Figure 1. 19: Equally stable state 1 and 2 under applied field in x-direction. [39]



1.7.2 Ways to reach field free switching

Various way can be used to fulfill field free switching by breaking the symmetry in different aspects. One of the common ways is lateral structural symmetry breaking. By wedging the FM (CoFeB[44]) or NM (Ta[42], Pt[43]) layer or a thin wedge light metal insertion [45], the symmetry in y-direction is broken, which the current will thus induces an effective field in z-direction. Since the induced field depends on the direction of current, certain direction of current will have a favor state, therefore, deterministic switching can be reach.

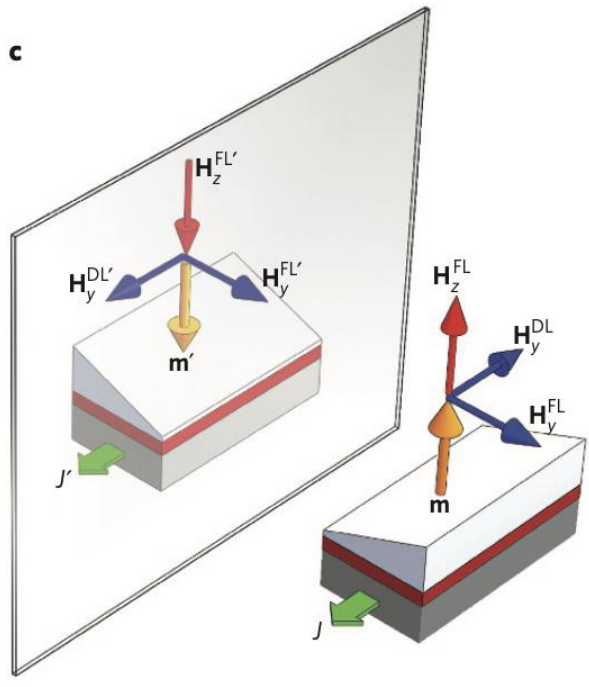


Figure 1. 20: Mirror symmetry of y-direction symmetry breaking. [42]

Another way to fulfill field free switching is through interlayer coupling. For example, an AFM layer is placed above the FM layer forming an AFM/FM interface. The exchange bias at the interface plays the role of an in-plane field to break the symmetry. After field

annealing [46] or sputtering under an in-situ field[47], the perpendicularly magnetized FM layer will tilted by the exchange bias and field free switching can then be reach.

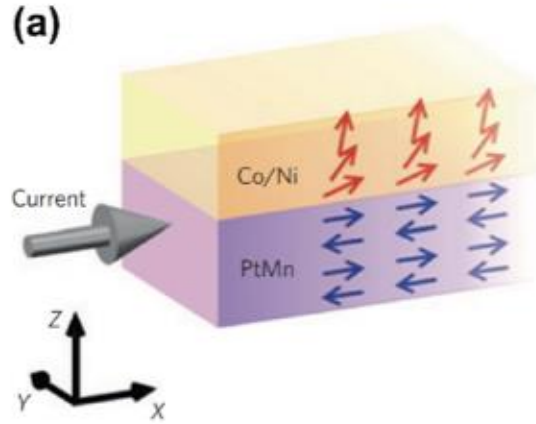
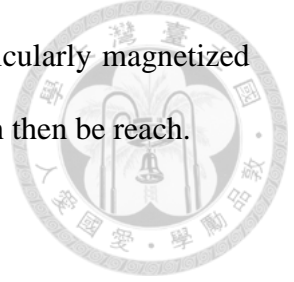


Figure 1. 21: Illustration of exchange bias in Co/Ni/PtMn system. [46]

Other than mirror symmetry, breaking the chiral symmetry is another aspect to fulfill FSS, which is usually done by introducing Dzyaloshinskii-Moriya interaction (DMI) [48]. DMI is an exchange interaction between neighboring spins S_i and S_j , which its Hamiltonian H_{ij} can be describe as

$$H_{ij} = D_{ij} \cdot (S_i \times S_j) \quad (1.8)$$

where D_{ij} represents the DMI tensor. The DMI will lead to chiral spin texture (Fig 1.22), with certain current direction and a given DMI, a specific texture is preferred due to the lower DMI energy. Therefore, the magnetization direction is decided by current and FSS can be fulfilled.

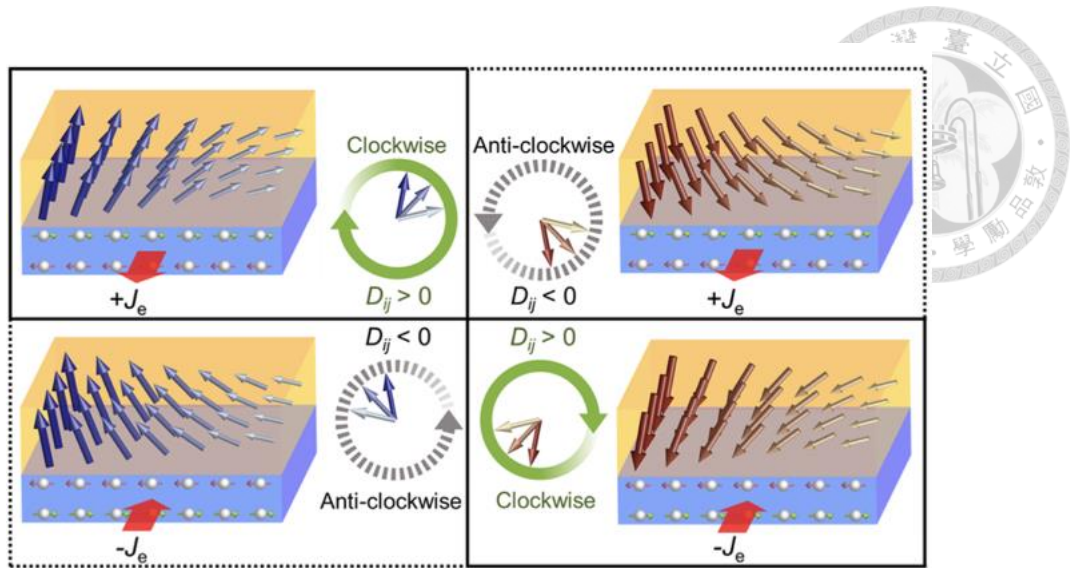


Figure 1. 22: Four possible non-collinear spin textures given by DMI.[46]

1.8 Motivation of this work

Compared to STT-MRAM which rely on spin polarization current, SOT-MRAM utilizes SOT to switch the magnetization, giving it various of advantages such as faster writing speed, lower energy consumption, lower data loss, longer lifespan etc... For SOT-MRAM, finding a way to fulfill deterministic current induced magnetization switching is crucial in industrial applications[49]. Field free switching can be realized by several ways including lateral symmetry breaking (wedge), chiral symmetry breaking (DMI) and interlayer coupling (exchange bias). In this work, I studied the effect and evaluate the switching ratio when wedging different layer in Ta/Pt/Co/Pt/Ta PMA system, including combination of wedge layers with different directions. The anneal process is also conduct on the wedge sample to observe the enhancement of SOT.

Chapter 2 Experiments



2.1 Hall bar fabrication

2.1.1 Photolithography

To facilitate electrical measurements of the magnetic thin film, we have fabricated the device in the shape of a double cross Hall bar. First, the substrate is baked to remove the moisture at 373K. Then the positive photoresist is carefully dripped on the wafer and put on the spin coater to form a uniform photoresist film. The photoresist should be retreat to room temperature before use. After spin coating, the wafer is baked again to dry out the solvent and release the stress of the film. UV exposure will increase the dissolution rate of the positive photoresist in the developer (TMAH). After the exposed photoresist is washed off by TMAH and DI water, the pattern of mask will be transfer to photoresist on the substrate.

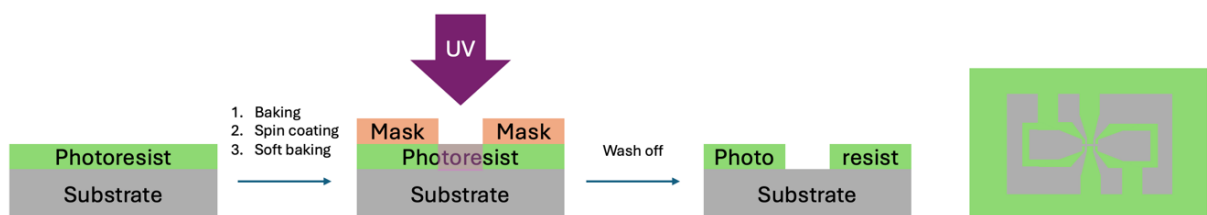
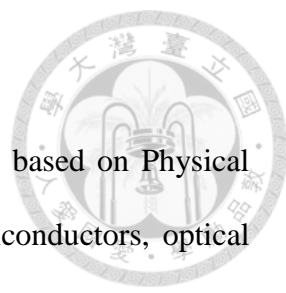


Figure 2. 1: Process of photolithography of the Hall bar pattern.

2.1.2 Magnetron sputtering



Magnetron sputtering is a common vacuum coating technique based on Physical Vapor Deposition (PVD), widely used in the manufacture of semiconductors, optical components, and various surface coatings. First, the substrate with Hall bar pattern are placed in a vacuum chamber. The air in the chamber is evacuated to reduce impurities and gas molecules, enhancing the quality and adhesion of the coating. After the pressure decrease to 1×10^{-7} , Argon gas is introduced into the vacuum chamber to generate ions. A voltage difference is created between the target material and the substrate, forming plasma. In the plasma, gas molecules are ionized into positive ions and free electrons by electron impact. A strong magnetic field is configured around the target material to control the motion of electrons, increasing the collision probability of ions and electrons on the target surface, thereby enhancing the deposition rate. The positive ions are accelerated by the electric field towards the negatively charged target material and bombard it. This high-energy bombardment causes atoms from the target material's surface to be ejected (sputtered), which then fly towards the substrate and condense on its surface to form a film. By controlling parameters such as sputtering time, power, and gas pressure, the film's thickness and properties can be precisely controlled. After sputtering, the substrate is soaked in toluene and vibrate in ultrasonic cleaner to remove the photoresist.

In this thesis, all the materials are deposited on the thermally oxidized Si wafer at room temperature, with DC power 30W and the working pressure of argon is 3 mTorr. The substrate holder rotates at 10 rpm and the rotation is turn off when depositing wedge layers.

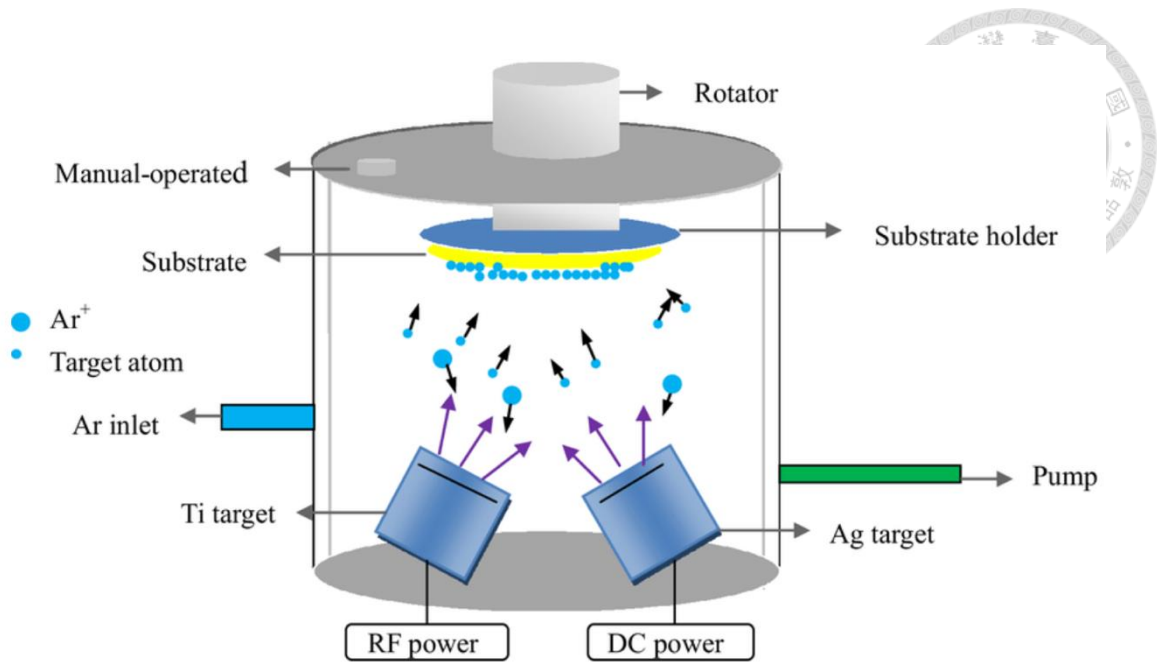


Figure 2. 2: Illustration of magnetron sputtering. [50]

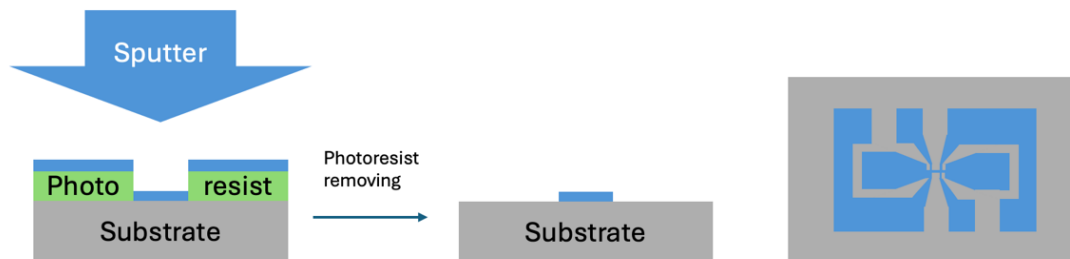


Figure 2. 3: Lift off process.

2.2 Measurement methods

2.2.1 Loop shift measurement

Loop shift measurement is used to extract the damping like torque efficiency ξ_{DL} and the DMI effective field H_{DMI} in PMA films. In FM layer, Néel domain wall (DW) separates magnetic moment in different direction, while DMI stabilizing it. The SOT

exerted by SHE will effect on the DW moment and become an effective field perpendicular to the PMA film (H_{eff}^z). Without an in-plane field H_x , the moments will not tilt in certain x direction, result in opposite direction of neighboring DW moments, which the DWs move simultaneously so the domain does not expand (Fig 2. 4a). On the contrary, the moments will be tilted in same x direction when H_x is applied and the H_{eff}^z will point in same direction, the domain will then be expanded (Fig 2. 4b).

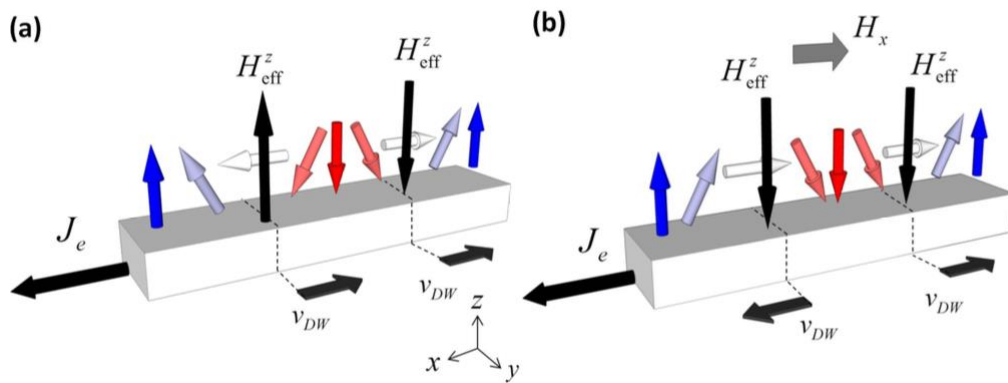


Figure 2. 4: Illustration of Néel DW motion of a PMA heterostructure (a)with and (b)without H_x . [51]

The experiment setup is shown in Fig. 2. 5a. A dc current I_{DC} and an in plane magnetic field H_x is applied along the x direction. Sweeping the out of plane field H_z and measuring the cross voltage will result in a hysteresis loop as shown in Fig. 2. 5b. By applying different I_{DC} , the hysteresis loop will “shift” and the dependence of H_{eff}^z and I_{DC} can be extracted as shown in Fig. 2. 5c. When larger H_x is applied, the slope H_{eff}^z/I_{DC} will eventually saturate when H_x overcome DMI field, and the value is related to the SOT efficiency χ_{SHE} , as shown in Fig. 2. 5d.

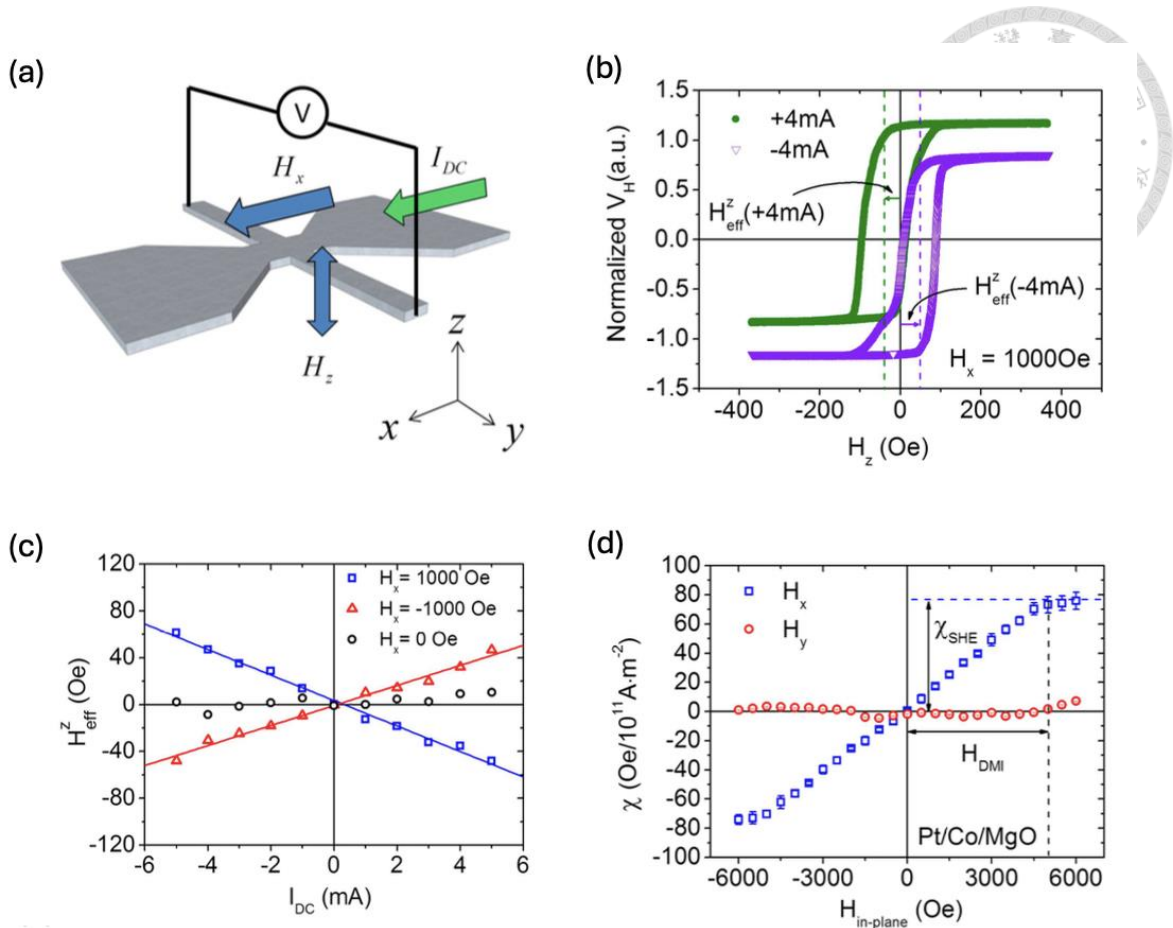


Figure 2. 5: (a) Setup of hysteresis loop shift measurement. (b) Hysteresis loop of Pt(4)/CoFeB(1)/MgO(2) sample with $I_{DC} = \pm 4$ mA and $H_x = 1000$ Oe. (c) H_{eff}^z vs I_{DC} under different H_x of Pt(4)/CoFeB(1)/MgO(2) sample. (d) χ as a function of applied H_x for Pt(4)/Co(1)/MgO(2). [51]

2.2.2 Current-induced SOT field-free switching measurement

The experiment setup is same as the loop shift measurement (Fig. 2. 5a) but the applied field provided by 5204 projector vector field magnet from GMW associates [52], H_x and H_z , are removed. The write current is provided by Keithley 2400 sourcemeter and the Hall voltage is measure by Keithley 2000 multimeter. By sweeping the write current I_{write} , current induced SOT will switch the magnetization in FM layer, forming a hysteresis loop as shown in Fig. 2. 6. From the loop we can obtain the critical switching current which is the minimum I_{write} to switch the magnetization and ΔR which is

difference of resistance between opposite magnetizations. The switching ratio can be calculated as

$$\frac{\Delta R_{field\ free}}{\Delta R_{field}} \times 100\% \quad (2.1)$$

which represents the ability and efficiency of achieving magnetic state transitions without the assistance of an external magnetic field.

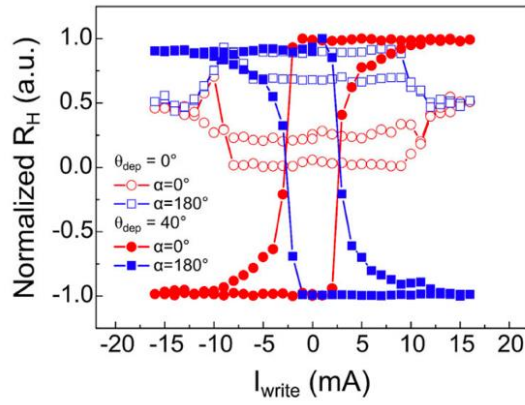


Figure 2. 6: Representative field-free switching loops for Pt/Co/Pt wedge system. [43]



Chapter 3 Result

Due to the perpendicular magnetization direction, magnetic heterostructure with PMA is considered to have multiple advantages such as higher stability to heat, larger storage density and scalability. Also, as former mentioned, symmetry breaking is critical for fulfilling field free switching in SOT-MRAM. There are various ways to break the symmetry and a simple reach is wedge deposition in magnetic heterostructure, which has low fabrication difficulty. Therefore, a simple magnetic heterostructure with PMA, Ta(1)/Pt(2)/Co(0.8)/Pt(1)/Ta(2), is chosen, as shown in Fig. 3. 1. Inspired by Hu's work [43] which investigate the relation between tilted anisotropy and wedge Pt buffer layer, we further dig in the influence of wedging every layer from seeding layer to capping layer. We also discovery the probability to combine multiple wedge layers with different directions.

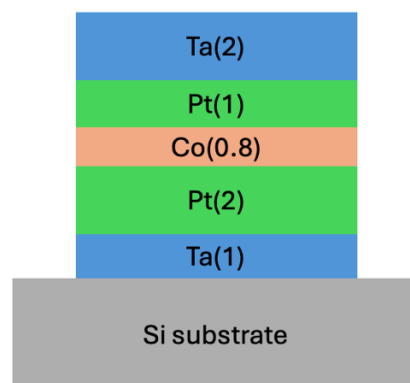


Figure 3. 1: Schematic illustration of the Ta/Pt/Co/Pt/Ta layer stack.



3.1 SOT characterization of control sample

First, current-induced SOT-driven magnetization switching measurement is utilized to characterize the basic properties of SOT switching of the control sample with full rotation depositing (No wedge). The AH loop measurement under $I_{DC} = 1$ mA, H_z sweeping between ± 300 Oe is shown in Fig. 3. 2a where Hall resistance $R_H=5.3$ Ohm and $H_C= 114$ Oe. The relation between H_z^{eff} and I_{DC} under $H_x=\pm 500$ Oe is shown in Fig. 3. 2b, clearly showing a linear behavior. Relation between the slope H_z^{eff}/I_{DC} and in-plane field H_x is shown in Fig. 3. 2c, indicate that the loop shifts in opposite direction when positive and negative H_x is applied. The saturation value of the slope $H_z^{eff}/I_{DC} = 8.3$ Oe/mA is extracted when H_x reaches 600Oe, which pointed out the overcoming of H_{DMI} by the applied field.

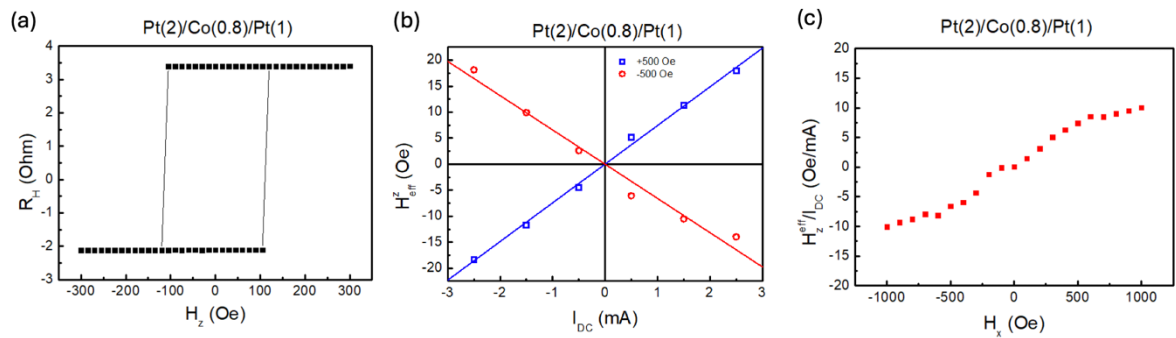


Figure 3. 2: SOT characterization of Ta(1)/Pt(2)/Co(0.8)/Pt(1)/Ta(2) control sample. (a) AH loop result. (b) H_z^{eff} as a function of I_{DC} under $H_x=\pm 500$ Oe. (c) H_z^{eff}/I_{DC} as a function of H_x .

The wedge sample is then fabricated by magnetron sputtering, since the plane normal of target and substrate holder is not parallel, stopping the rotation of substrate holder will result in an oblique deposited film. The wedge deposition direction is perpendicular to the current in order to break the symmetry. The AH loops of different wedge layers are

measured and the coercive field H_C and ΔR_H is shown in Fig 3. 3, indicates that wedging a certain layer does not change the loop properties significantly.

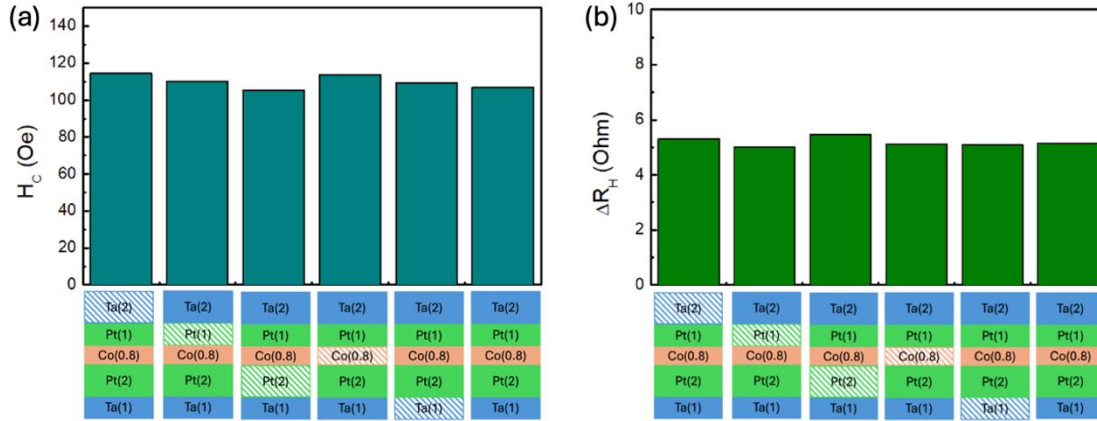


Figure 3. 3: (a) H_C comparison of different wedge layers. (b) ΔR_H comparison of different wedge layers.

3.2 Current-induced SOT field-free switching of single wedge layer

In order to demonstrate the field free switching behavior, the experiment was conducted in an environment without any potentially impactful external magnetic field. The setup of the experiment is illustrated in Fig. 3. 4. Note that the yellow arrow indicates the wedge direction from near to far. The result of current induced SOT field free switching of different wedge layers is shown in Fig. 3. 5. For wedge Pt samples, both upper and bottom Pt wedge performs clear switching loop in opposite writing current direction, manifested a deterministic field free switching behavior with a ~50% switching ratio for bottom Pt wedge and ~65% switching ratio for upper Pt wedge. Both have a critical switching current ~11mA. For wedge seeding Ta, the switching loop is also clear

and perform deterministic field free switching at a switching ratio $\sim 50\%$, however, compared to wedge Pt samples, the critical switching current is almost twice as high which was as expected since Ta layer is distanced from the Pt/Co interface. As for control sample, wedge Co and wedge capping Ta sample, no field free switching is observed since the switching ratio is almost 0 and cannot accomplish deterministic switching.

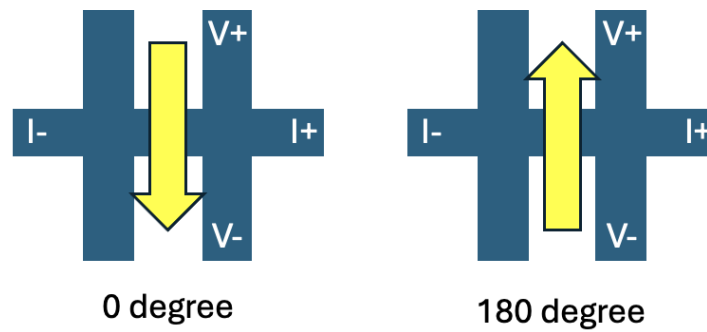


Figure 3. 4: Experimental setup of current-induced SOT field-free switching measurement.

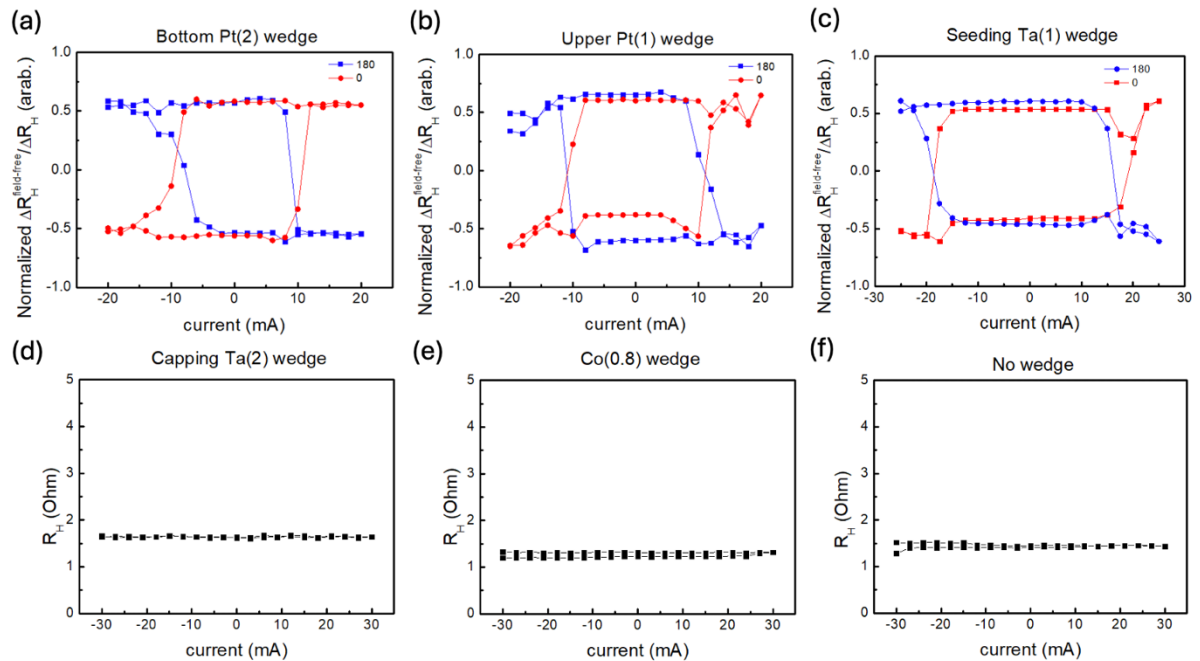


Figure 3. 5: Representative current induced field free SOT switching loops for (a)wedge bottom Pt layer, (b)wedge upper Pt layer and (c)wedge seeding Ta layer samples. Field free switching measurements for (d)wedge capping Ta, (e)wedge Co and (f)control sample.

3.3 Tilted PMA characterizing of single wedge layer

To observe the miniature deviation of the perpendicular magnetic easy axis, fixed current AHE loop shift measurement with different in plane magnetic field direction is applied. If the magnetic anisotropy easy axis is ideally perpendicular to the film, the AH loop will not shift since the applied in plane field is unable to project onto the vertical easy axis. In the other hand, the slightly tilted easy axis will reflect the in plane magnetic field resulting in loop shifting. To avoid the effect of Joule heating, applied current for AHE is set to 0.1mA. To find out the direction of tilted anisotropy precisely, the azimuthal angle ϕ_{ani} and polar angle θ_{ani} must be extracted. We can calculate from the loop shift results, the total magnetic field on the easy axis H_{ea} is the sum of the projection of z direction field H_z on the easy axis and the projection of in plane field H_{IP} on the easy axis [43]. That is

$$H_{ea} = H_z \cos\theta_{ani} + H_{IP} \cos(\theta_{ani} - \phi_H) \sin\theta_{ani} \quad (3.1)$$

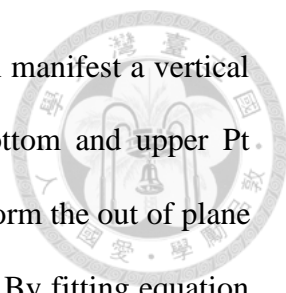
By AHE loop we define the shift of loop center ΔH_{SW} as

$$\Delta H_{SW} \equiv \frac{(H_{SW}^{down\ to\ up} + H_{SW}^{up\ to\ down})}{2} \quad (3.2)$$

On the easy axis, the magnitude of magnetic field required to shift from up to down and from down to up should be equal, therefore, loop center shift ΔH_{SW} should be in proportion to the in plane magnetic field H_{IP} , the relation can be organized into

$$\begin{aligned} \frac{\Delta H_{SW}}{H_{IP}} &\equiv \frac{(H_z^{down\ to\ up} + H_z^{up\ to\ down})}{2H_{IP}} \\ &= -\cos(\phi_{ani} - \phi_H) \tan\theta_{ani} \end{aligned} \quad (3.3)$$

The linear relation between ΔH_{SW} and H_{IP} with respect to different in plane field angle is shown in Fig. 3. 6. For the control sample without wedge deposition, H_{IP} with 90° lies



along $\Delta H_{sw} = 0$ Oe, indicate that no shift of out of plane loop which manifest a vertical magnetic easy axis. In contrast, for wedge seeding Ta, wedge bottom and upper Pt samples which present deterministic field free switching clearly perform the out of plane loop shifting, indicating the presence of a tilted magnetic easy axis. By fitting equation 3.3 and the slope $\frac{\Delta H_{SW}}{H_{IP}}$, as shown in Fig. 3. 7, ϕ_{ani} and θ_{ani} of the tilted PMA of different wedge layers are extracted. The comparison of ϕ_{ani} and θ_{ani} with different wedge layers is shown in Fig. 3. 8. Note that the direction of tilted magnetic anisotropy is similar for both upper and bottom Pt wedge samples, with $\phi_{ani} \sim 60^\circ$ and $\theta_{ani} \sim 15^\circ$. In Hu's work[43], ϕ_{ani} is measured to increase with deposition angle of Pt and could eventually reach 80° . Since we did not adjust the deposition angle in this experiment, the result is reasonable. As for seeding Ta wedge sample, ϕ_{ani} is almost 90° which is thought to be wedge deposited ideally. The θ_{ani} of wedge Ta sample is also the largest of all ($\sim 20^\circ$). We assume that since Ta layer is the first to be deposited, it will tilt the structure of entire film and the magnetic anisotropy.

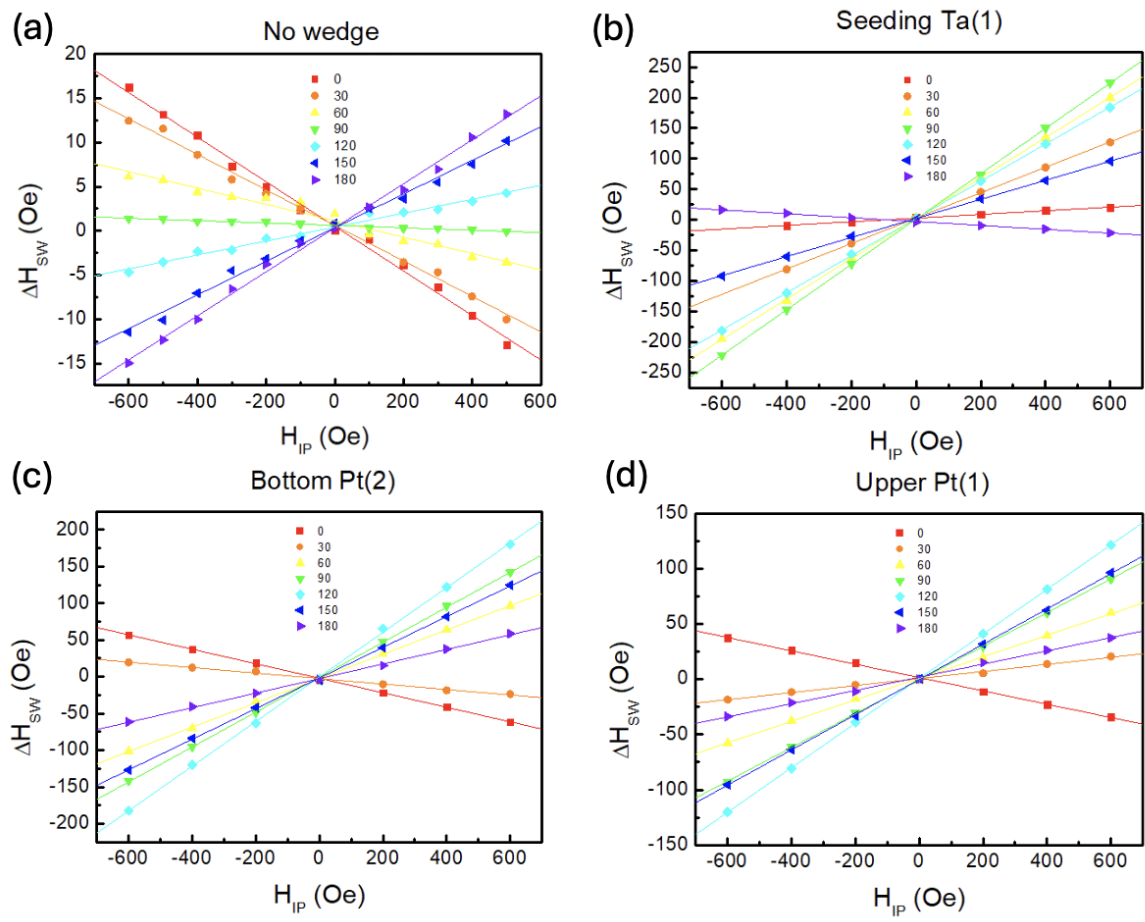


Figure 3. 6: Linear relation between switching field ΔH_{sw} and in plane magnetic field H_{IP} scanning in different in plane field angle of (a)control sample, (b)wedge seeding Ta layer, (c)wedge bottom Pt and (d)wedge upper Pt.

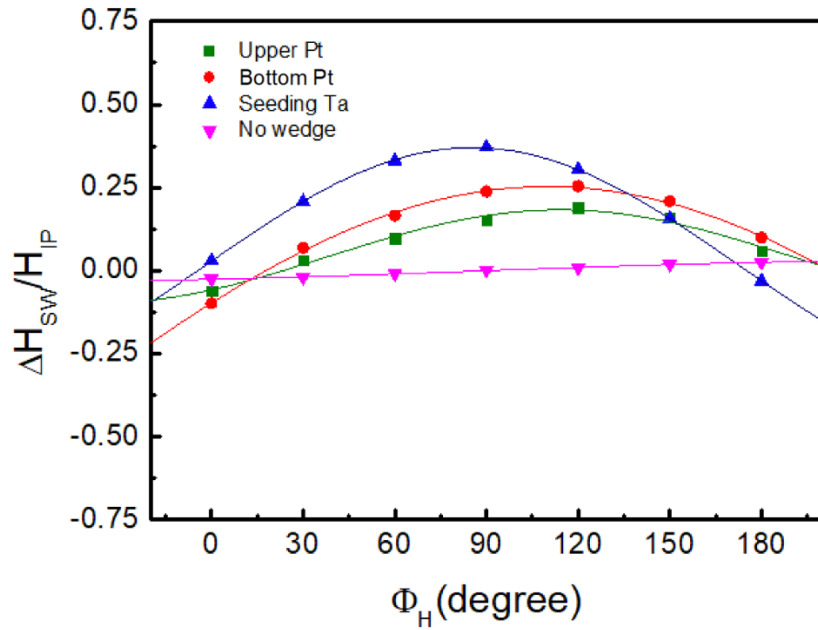


Figure 3. 7: Sinusoidal relation between $\frac{\Delta H_{SW}}{H_{IP}}$ and ϕ_H of upper Pt wedge, bottom Pt wedge Seeding Ta wedge and control sample, fitting by equation 3.3.

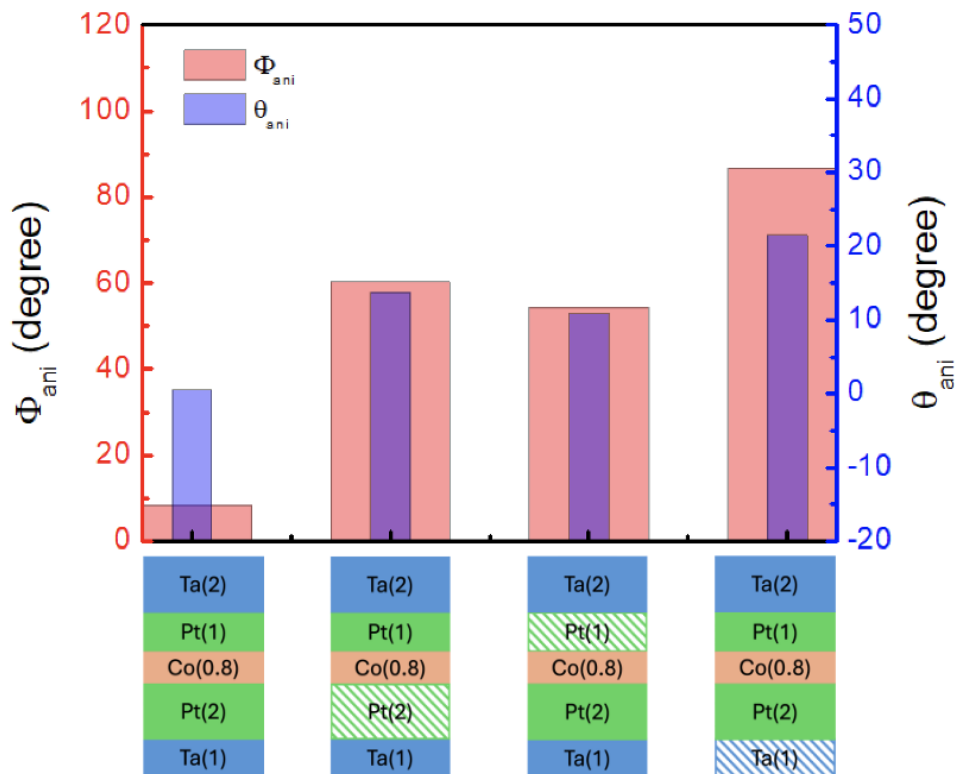


Figure 3. 8: Comparison of the azimuthal ϕ_{ani} and polar angle θ_{ani} of tilted anisotropy of upper Pt wedge, bottom Pt wedge, Seeding Ta wedge and control sample.

3.4 Parallel and antiparallel wedge Pt layer



After the influence of wedging each layer in Ta/Pt/Co/Pt/Ta magnetic heterostructure at once is characterized, inspired by Huang's work in interlayer DMI [53], we further the outcome of combining Pt wedge layers with parallel and antiparallel wedge directions. The schematic illustration of parallel and antiparallel wedge Pt is shown in Fig. 3. 9a, note that the red arrow represents the direction of deposition. The hysteresis loop shift measurement is adopted and the H_z^{eff}/I_{DC} with respect to H_x is shown in Fig. 3. 9b. The slightly drop in H_z^{eff}/I_{DC} of antiparallel wedge Pt sample might be due to the impurity in fabrication process. Since the rotation of the substrate holder cannot be controlled precisely, the antiparallel sample is taken out of the chamber to rearrange the substrate in order to deposit the upper Pt layer in an opposite direction.

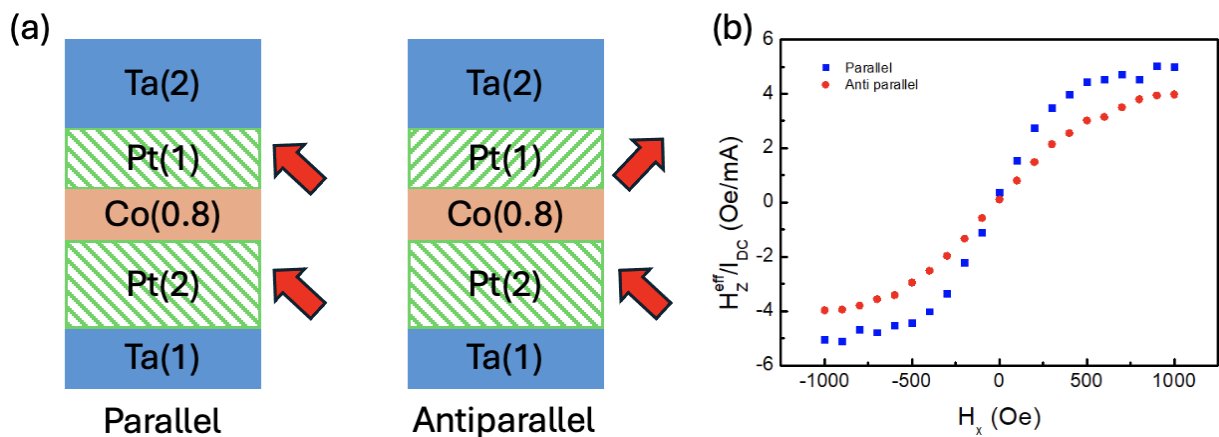


Figure 3. 9: (a) Schematic illustration of parallel and antiparallel wedge Pt magnetic heterostructures. The red arrow is the direction of wedge deposition. (b) H_z^{eff}/I_{DC} with respect to H_x f parallel and antiparallel wedge Pt samples.

Current induced SOT field free switching measurement is conducted, and the result is shown in Fig. 3. 10. Both parallel and antiparallel wedge Pt samples perform clear switching loop in opposite writing current directions, indicate a deterministic field free switching. For parallel wedge sample, the field free switching ratio can reach 73% which is small improvement compared to upper Pt wedge. The critical switching current is 5mA,

showing a significant 50% reduction to single Pt wedge samples. For antiparallel wedge sample, the critical switching current remains low at 5mA, but the switching ratio decreases to 25%. A noticeable point is that the switching polarity of antiparallel wedge is opposite to parallel wedge and other single wedge Pt samples, which will be explained later.

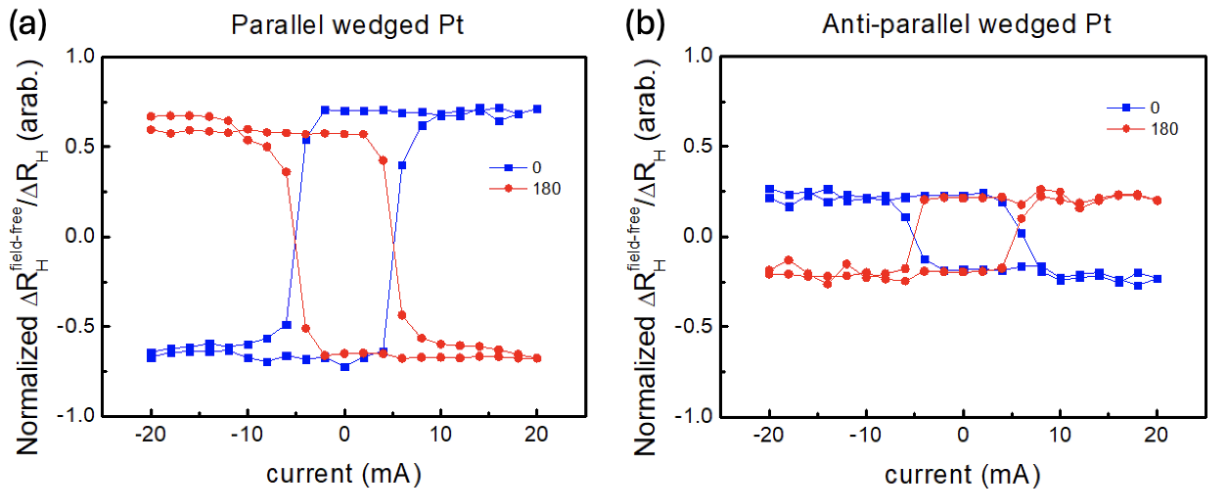


Figure 3. 10: Representative current induced field free SOT switching loops for (a) parallel wedge Pt layers and (b) antiparallel wedge Pt layers.

We further conduct the fixed current loop shift measurement with different in plane magnetic field to characterize the tilted anisotropy of parallel wedge Pt sample. The sinusoidal relation between $\frac{\Delta H_{SW}}{H_{IP}}$ and ϕ_H is shown in Fig. 3. 11, and the comparison of azimuthal ϕ_{ani} and polar angle θ_{ani} is summarized in Fig. 3. 12. Note that ϕ_{ani} is same compared to upper and bottom wedge Pt sample while θ_{ani} is slightly larger which reflect the increment of field free switching ratio. The enhancement of the θ_{ani} is as expected since the tilted magnetic anisotropy is strongly dependent on the crystalline texture, that is, the PMA is form by the Pt (111) texture in Pt/Co and by our result, in

Co/Pt as well [54][55]. Therefore, parallel wedge Pt sample forms the tilted Pt (111) texture at the bottom Pt layer, then, repeat at the upper Pt. Will result in the enhancement of overall tilted texture in Pt/Co/Pt system and the consequent of larger θ_{ani} . In the other hand, the contribution of two upper and bottom Pt wedge layer in tilted texture will compete since they are deposited in opposite direction. The mechanism is illustrated in Fig. 3. 13, note that the iron gray arrow represents the direction of tilted texture, and the purple arrow represents the direction of the tilted magnetic anisotropy. As former mentioned, the switching polarity is opposite for the antiparallel wedge sample. The reason is in the specific situation, the contribution of the upper wedge Pt overcome the bottom Pt, forming a negative polar angle θ_{ani} . The polar angle θ_{ani} is then balanced out by the competence of upper and bottom wedge Pt layers.

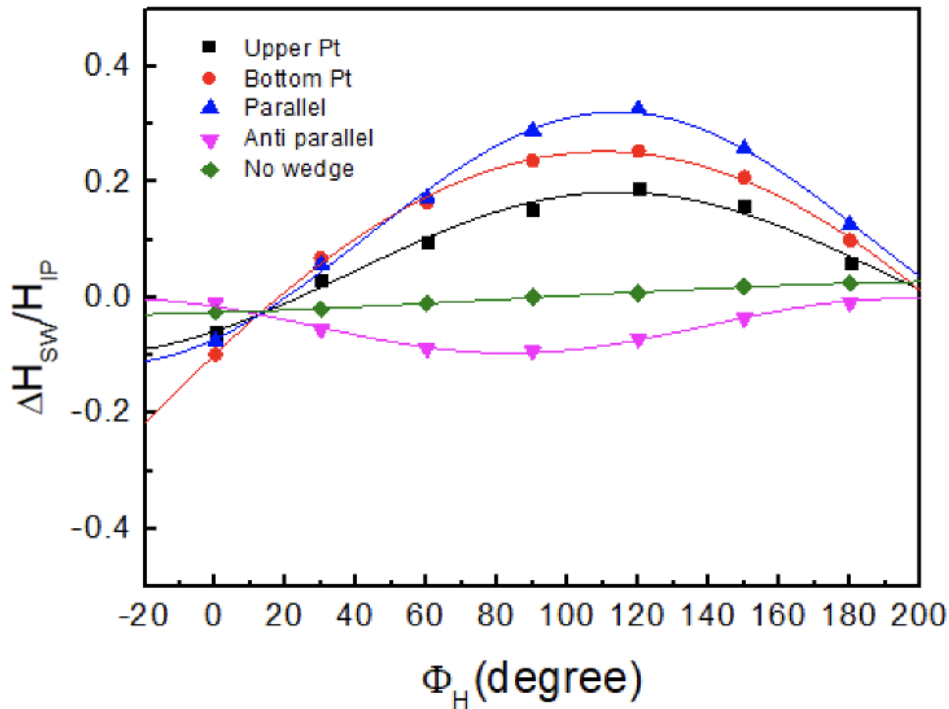


Figure 3. 11: Sinusoidal relation between $\frac{\Delta H_{SW}}{H_{IP}}$ and ϕ_H of no wedge, upper Pt wedge, bottom Pt, parallel wedge Pt and antiparallel Pt sample, fitting by equation 3.3.

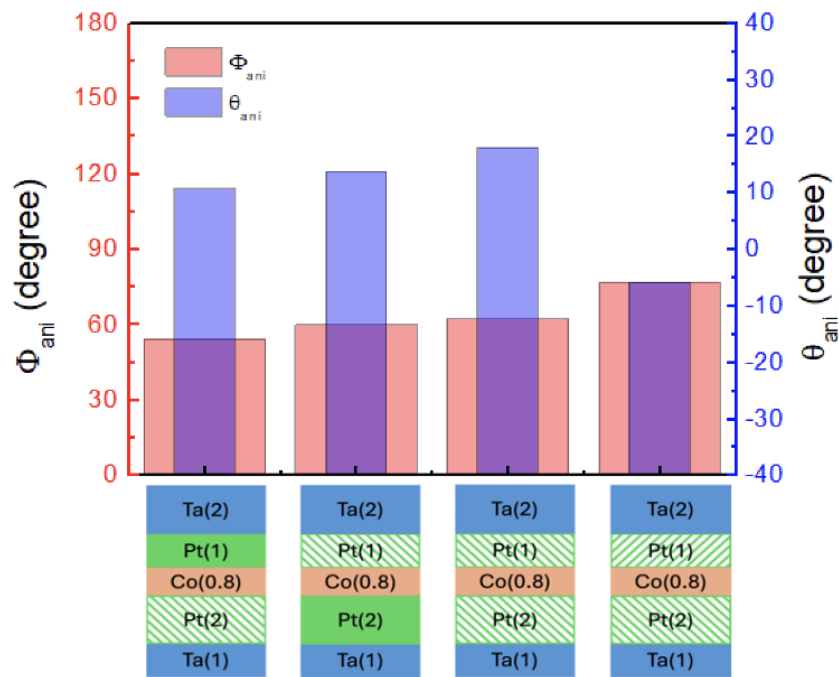


Figure 3. 12: Comparison of the azimuthal ϕ_{ani} and polar angle θ_{ani} of tilted anisotropy of upper Pt wedge, bottom Pt wedge, parallel wedge Pt and antiparallel wedge Pt sample.

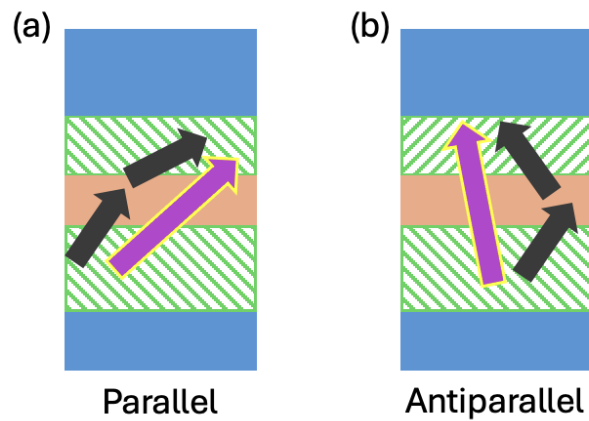


Figure 3. 13: Schematic illustration of the mechanism of tilted crystalline texture induced magnetic anisotropy of (a) parallel wedge Pt and (b) antiparallel wedge Pt.



3.5 Annealing effect on tilted PMA

For SOT magnetic tunnel junction, post deposition thermal annealing is considered a crucial process to improve the properties including the PMA, spin injection efficiency, tunnel magneto resistance ratio and the critical switching current [56][57]. Therefore, thermal annealing is carried on bottom Pt wedge sample to observe the annealing effect on field free switching and the magnetic easy axis. The annealing profile is set at 300° for 30 minutes to prevent the elimination of PMA. The AH hysteresis loop is shown in Fig. 3. 14a, note that the hysteresis loop is clear which indicate the presence of PMA, however, the coercive field H_C drops about 50% after the annealing. H_z^{eff}/I_{DC} with respect to H_x is shown in Fig. 3. 14b, the SOT behavior remains the same after thermal annealing.

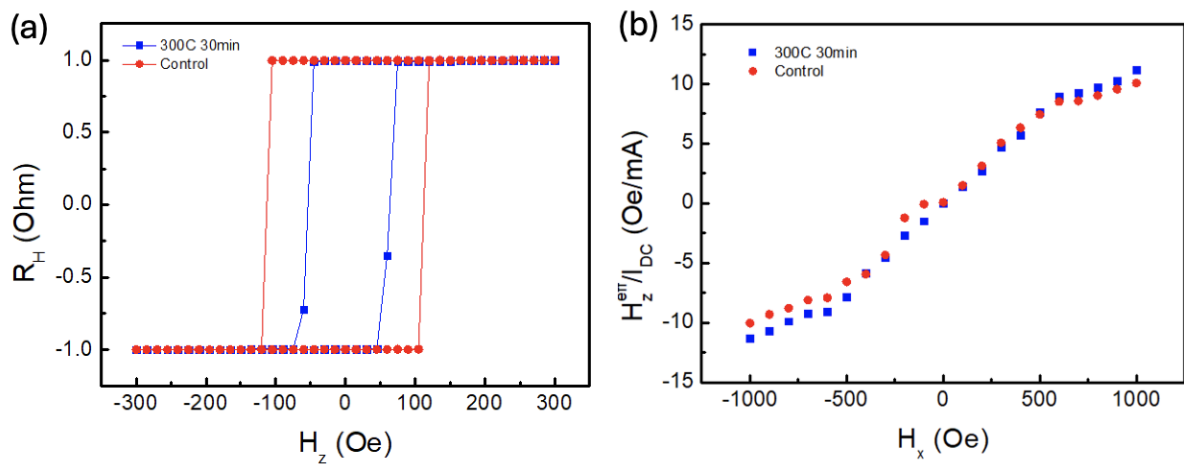


Figure 3. 14: (a) Hysteresis AH loop and (b) H_z^{eff}/I_{DC} as a function of H_x of bottom Pt wedge sample before and after thermal annealing.

Current induced SOT field free switching measurement is conducted, the representative switching loop is shown in Fig. 3. 15. The field free switching ratio of annealed sample decrease to 20% and the switching polarity is opposite to the control sample, which might be due to the remanence of the annealing instrument or the magnetization switches partially. Fixed current loop shift measurement with different in

plane magnetic field is conducted to further investigate the influence on tilted magnetic anisotropy due to thermal annealing. The sinusoidal relation between $\frac{\Delta H_{SW}}{H_{IP}}$ and ϕ_H of annealed bottom Pt wedge sample is shown in Fig. 3. 16. $\frac{\Delta H_{SW}}{H_{IP}}$ is almost zero for all the ϕ_H , forming a curve with minute amplitude, indicate the magnetic easy axis is almost perpendicular to the film. The most possible reason is the atomic rearrangement and intermixing between layers sabotages the tilted texture of Pt (111), causing the magnetic anisotropy to reset to the perpendicular direction [43][58][59]. It will be a challenging task to preserve the tilted PMA after thermal annealing or even strengthen the anisotropy by specific annealing process.

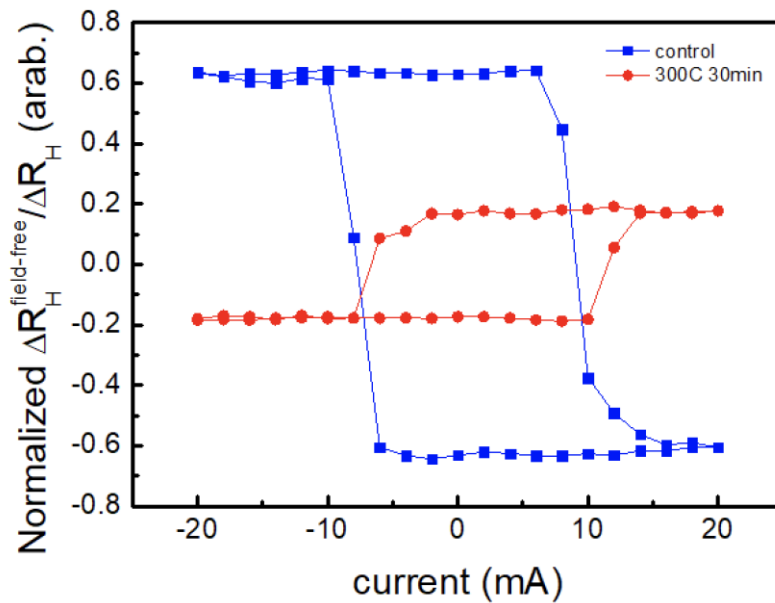


Figure 3. 15: Representative current induced field free SOT switching loops for bottom Pt wedge sample before and after annealing.

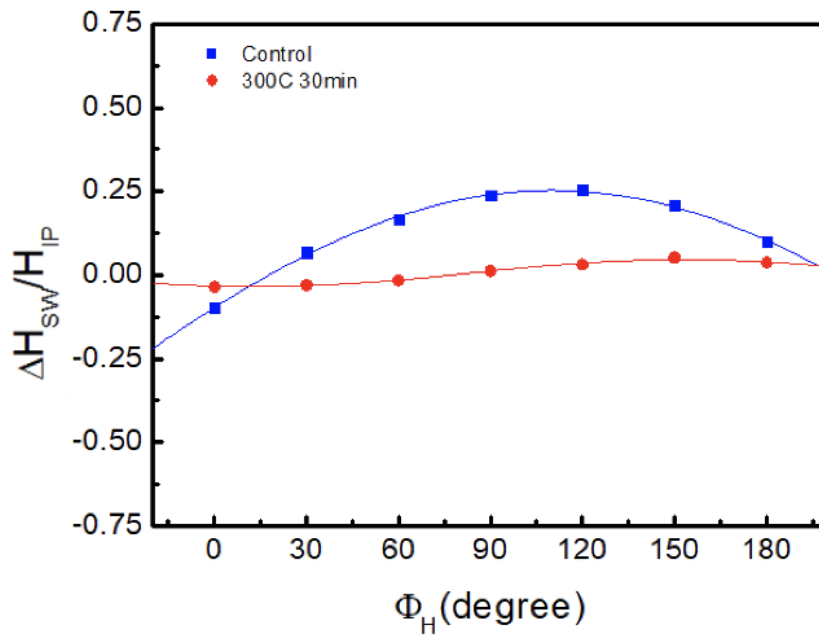
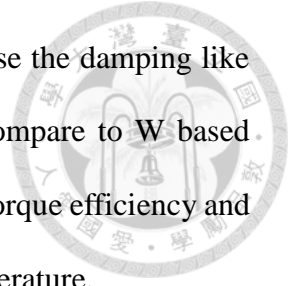


Figure 3. 16: Sinusoidal relation between $\frac{\Delta H_{SW}}{H_{IP}}$ and ϕ_H of bottom Pt wedge before and after thermal annealing, fitting by equation 3.3.

3.6 Challenges

To further utilize this structure as the free layer into practical magnetic tunnel junction (MTJ) fabrication, several ordeals must be overcome. The great spin Hall properties and good conductivity of Pt based alloys make it a competitive candidate in replacing W in CoFeB/MgO based MTJ, however, due to the lattice mismatch between Pt (FCC) and CoFeB/MgO (BCC) after thermal annealing, the PMA will be destroyed in 400°C, which is the standard temperature of back end off line (BEOL) process of CMOS fabrication. Work has reported that an insertion layer of FeTa between CoFeB and Co/Pt can improve the crystallinity of interface [60]. The crystal structure of FeTa can transform from amorphous to BCC or FCC after 400°C annealing, relying on the crystal structure of neighboring layer, which can greatly decouple the two different lattices. FeTa insertion layer also enhance the ferromagnetic coupling to strengthen the anisotropy. Another

reported way is to mix 3d transition metal into Pt, which can increase the damping like torque efficiency by OHE [61]. The experiment has shown that compare to W based structure, Pt-Cr based structures manifest competitive damping like torque efficiency and better power consumption after annealed in the standard BEOL temperature.



Chapter 4 Conclusion



Summarizing the thesis, every single layer in Ta/Pt/Co/Pt/Ta is deposited in wedge condition to test the ability of field free switching and characterize the tilted magnetic anisotropy. Hysteresis loop shift measurement is utilized to observe the SOT switching properties, point out that coercive field H_C and Hall resistance difference ΔR_H remains unchanged in various wedge layers. Current induced SOT field free switching is conducted to extract the switching ratio and critical switching current. Later on, we investigate the azimuthal angle ϕ_{ani} and the polar angle θ_{ani} of the tilted magnetic easy axis, which shows a consistent result to previous report. We further conduct the same electrical measurements on wedging the upper and bottom Pt in parallel and antiparallel directions. Parallel wedge sample manifests a larger θ_{ani} which reflects on the improvement of field free switching while the antiparallel wedge sample shows a decrease in switching ratio and the reverse of switching polarity. The most persuasive reason is the enhancement and competence of two separated Pt wedge layer with the same or opposite direction. The possibility of post deposition thermal annealing in wedge structure is discussed at last. Field free switching ratio decrease significantly, and the tilted anisotropy is sabotaged after the annealing. It is reasonable to believe that the atomic rearrangement and intermixing between layer originate from annealing intermingles the tilted Pt (111) texture.

This work investigates the contribution of each layer in heterostructure (Fig. 4.1, 4.2), the discovery of combining various wedge layers also point out more possibility in

tilted PMA SOT device fabrication. The preservation of tilted texture after thermal annealing will be a challenging task in the future.

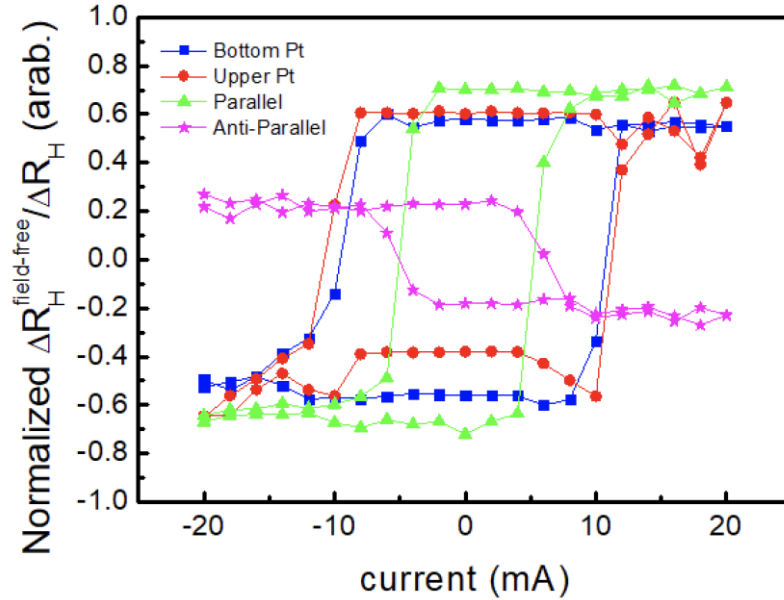
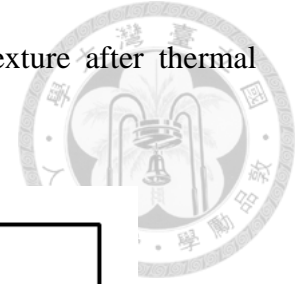


Figure 4. 1: Representative current induced field free SOT switching loops comparison for bottom Pt, upper Pt, parallel and antiparallel wedge samples.

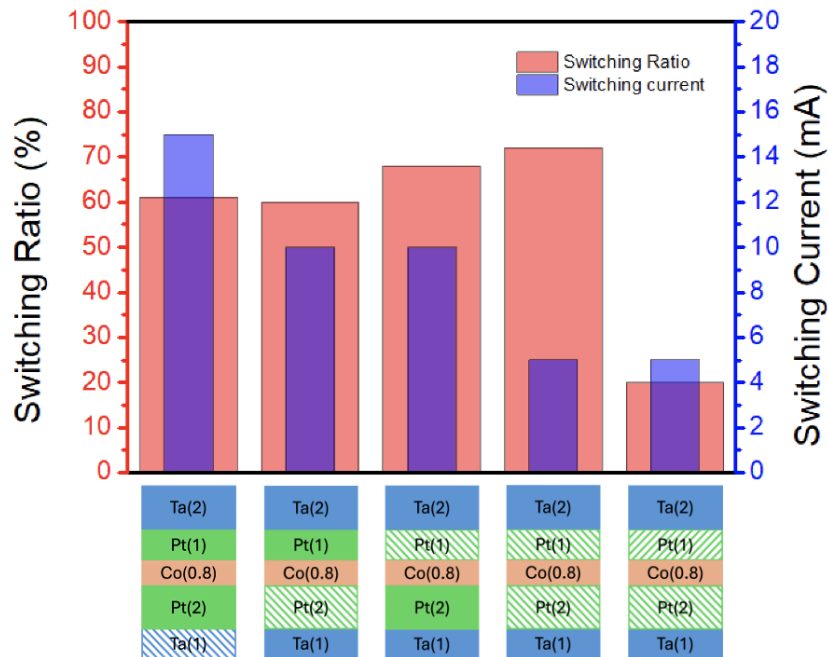
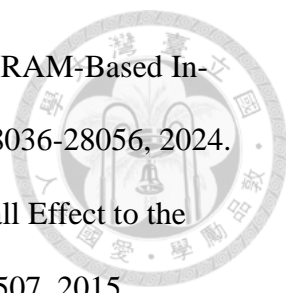



Figure 4. 2: Summary of field free switching ratio and critical switching current of seeding Ta, bottom Pt, upper Pt, parallel and antiparallel wedge samples.


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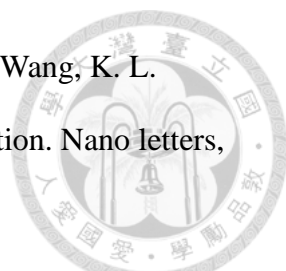
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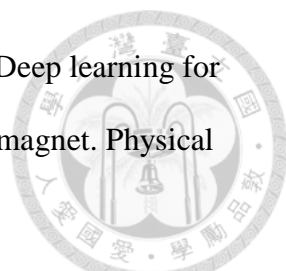
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