摘 要

本論文主要在探討鋨金屬的成長及加入磁性多層膜後之特性研究。當一層超薄的鋨 金屬層加在鈷鐵/鋨錳合金介面時, 其鈷鐵的矯頑場及磁滯曲線方正性可以在 400°C 退 火後還維持和初鍍膜狀態相近。此鈷鐵/鋨/鋨錳薄膜, 在歐傑電子縱深分析中, 亦可發 現鋨錳層內的錳原子並未擴散進入鈷鐵層, 此結果說明鋨金屬具有作為錳的擴散阻隔 層的潛力。

在非晶質的二氧化矽基板上成長鈷鐵/銥錳薄膜時, 需加入鋨金屬作為緩衝層, 方 可使得鈷鐵/銥錳薄膜成長出 fcc (111)指向, 並產生交換場。因為鋨為六方最密堆積結 構 (hcp), 其底面的(0002)面和 fcc 結構中的(111)面具有相同的原子排列方式,因此, 以銅作為種子層並藉由金屬-金屬磊晶成長法 (MMES method)可在氫終結的矽(100)及矽 (111)基板上, 成長出具有明顯 fcc (111)指向的鈷鐵/銥錳織構薄膜。當鍍製鈷鐵/銥錳 薄膜時, 鋨金屬在矽(100)及矽(111)基板上會形成不同的表面型態, 甚至, 銥錳在鈷 鐵/銥錳/鋨/銅/矽(100)中, 會隨著鋨的厚度增加, 而改變其晶體結構從(002)改變成 (111)。此具有較佳結晶性的鈷鐵/銥錳薄膜, 會形成較佳的磁滯曲線方正性, 而使得磁 矩的翻轉過程變得具有較佳的一致性。此鈷鐵/銥錳織構薄膜, 會於 250°C 得到最大交 換場並於 350°C 退火後使得其交換場消失, 相較於非織構的鈷鐵/銥錳薄膜, 其產生最 大交換場及交換場消失的溫度, 分別往上提升 50°C及 75°C, 另外, 當此織構鈷鐵/銥錳 薄膜的介面上再增加一超薄的鋨金屬層時, 亦可使得其退火後的交換場大於初鍍膜的 狀態。這些結果顯示, 藉由加入鋨緩衝層及鋨擴散阻隔層後, 鈷鐵/銥錳薄膜會得到較 佳的熱穩定性。

最後, 當選用適當的種子層, 具有高 hcp (0002)指向性且具有六重對稱性的鋨金 屬膜可以分別在室溫下以磁控濺鍍的方式成長於氫終結的矽(100)及矽(111)基板上。使

i

用銅金屬在氫終結的矽(100)基板上作為種子層, 可大幅將晶格常數的不匹配性自大於 30%降低至小於 7%, 而成長出具有雙晶結構且具有微弱六重對稱性的鋨金屬膜。此時可 觀察到一特殊的平面十二重對稱性, 來自於以[0002]方向為軸且彼此相差 90 度的磊晶 晶粒。另外, 當選用銅/金作為種子層時, 可在氫終結的矽(111)-1x1 表面上成長出具有 良好六重對稱結構的鋨金屬膜, 從其 XRD 的ϕ-san 中有六根高強度的繞射峰, 更可證明 此具有六重對稱性的鋨金屬膜之成長是可以被操控的。根據上述特性, 鋨金屬具有很高 的應用潛力且可於磁穿隧接面記憶胞製程及超大型積體電路製程間作為一重要的整合 媒介。

Abstract

This dissertation is mainly to study the growth of osmium (Os) and the properties of magnetic films with an Os layer. By insertion an ultrathin Os layer between CoFe/OsMn interface, the coercivity (H_c) and hysteresis squareness (S) of samples after annealing below 400°C can retain nearly the same value of that at as-deposited state. In the CoFe/Os/OsMn system, as revealed from the AES depth profile, the Mn atoms in OsMn layer did not enter the CoFe layer, and this result indicated the Os layer had potential to act as the diffusion barrier of Mn atoms.

The CoFe/IrMn films on $SiO₂$ substrate without Os buffer layer did not show the IrMn fcc (111) and the CoFe fcc (111) peaks and its exchange field (H_{ex}) is almost zero. Since Os is a hexagonal close-packed (hcp) metal and its basal (0002) plane has the same atomic arrangement of a (111) plane in fcc. When the Os layer deposited by metal-metal epitaxy on silicon (MMES) method with a Cu seed layer on the hydrogen-terminated Si substrate, the texture CoFe/IrMn could be grown, and a clear fcc (111) peak was observed. The Os layer on H-Si (100) and H-Si (111) shows different surface mesh for CoFe/IrMn growth. The structure of IrMn in CoFe/IrMn/Os/Cu/Si(100) can turn from (002) to (111) during increasing the thickness of Os layer. The much better crystallinity of the CoFe/IrMn showed better S, thus, the switching process of magnetization was more coherent. The textured CoFe/IrMn reached its $H_{ex. max}$ at 250°C, while the H_{ex} vanished at 350°C. Compared with the non-textured CoFe/IrMn, the 50 \degree C and 75 \degree C of improvement on the temperature at which the H_{ex,max} appeared and the H_{ex} disappeared were remarkable, respectively. For all the samples with an Os barrier, its CoFe/IrMn showed larger H_{ex} than that of the as-deposited state. These mean that a CoFe/IrMn film can have a better thermal stability with adding an Os diffusion barrier layer and an Os buffer layer.

Finally, by choosing the appropriate buffer layers, high-oriented hcp (0002) with 6-fold symmetry Os films can be grown on hydrogen-terminated Si (100) and Si (111) substrates by magnetron sputtering at room temperature, respectively. Using a Cu buffer layer, the lattice mismatch between Os (0002) and Si (100) was significantly reduced from $>30\%$ to \sim 7%, and thus Os films can grow with twin relationships and weak 6-fold symmetries. A 12-fold in-plane symmetry resulted from two sets of (0002) epitaxial grain rotated by 90 $^{\circ}$ with respect to each other along [0002] direction was observed. On the other hand, the Cu/Au buffer layer was selected to form an fcc (111) surface mesh on H-Si (111) -1x1. The 6 high intensity peaks of XRD φ scan diffraction were measured and which indicated the 6-fold Os (0002) can be well controlled. According to the properties mentioned above, Os do have high application potential and play an important role on integrating the ULSI and MTJ processes.

誌 謝

光陰荏苒, 轉瞬即將走完這段求學生涯, 回首這四年多來, 首先, 我要感謝指導 教授陳三元老師, 感謝您讓我追尋自己的興趣, 投入spintronics這個領域做研究, 並 且在各方面都給予我最大的支持與鼓勵, 讓我能順利完成這篇論文。再者,更要感謝另 一位指導老師-中央研究院物理所姚永德教授, 感謝您在研究方向的大力指導, 讓我擁 有許多的研究資源, 更在就學期間的論文發表上, 給予相當多寶貴的意見, 使我一路 走來倍感順利。當然, 工研院電光所的盧志權經理在實驗設備及實驗構想上的全力支持, 讓我能夠天馬行空的放手去嘗試我的構想, 更是催生這篇論文不可或缺的關鍵人物。另 外, 亦衷心感謝諸位口試委員對本論文所給予的指導與建議。

能夠完成這篇論文, 除了感謝三位老師無私的付出, 也要感謝在這四年中所有給 予過我幫助的人們: 感謝中研院幫忙作TEM試片的國龍以及幫忙作VSM的凱澤, 感謝中 正大學物理所幫忙作VSM的晃暐及軍浩,感謝在組裝濺鍍系統時給予大力幫忙的朱聰明 學長及富強, 以及太多太多相關的人們, 或許無法一一寫下你們的名字, 但是沒有你 們, 我是無法完成這篇論文的, 再次獻上我誠摯的感激。

求學生涯的多彩多姿當然少不了陪伴在我身邊的朋友們, 感謝工研院自旋科技實 驗室患難與共的各位夥伴: 瀛文、國瑞、正旭、建宏、藍青、怡昕、世斌、明道、哲榮 、維志及瑞峰, 不論在實驗上還是日常生活,因為你們才豐富了這段求學生涯, 若不是 你們陪在身邊, 真不知道該怎樣排解實驗上所遭遇的挫折與分享發表論文的喜悅; 還 有交大實驗室的邦強、晉慶、昆和、繼聖、定宇、彥好、白嘉、若豪、書萍、泓洲、小 秀,難忘每次與你們聚會時的歡樂氣氛; 另外, 還要感謝台大材料所的群淵,不論出國 開會、交換實驗心得, 在在都從你身上獲益良多。

最後, 特別要將此篇論文獻給我親愛的父母, 感謝你們自小到大的悉心栽培,也要 謝謝所有關心我的親朋好友,更要將這篇論文獻給這千多個日子來, 無怨無悔的陪在我 的身邊, 分享無數歡笑淚水、伴我走過低潮的摯愛-瑋寒。

泰彦 丁亥年 三月

v

Contents

References 105

Publications List 114

List of Tables

List of Figures

- Fig. 2-1 (a) Magnetization curve and (b) MR curve of the pseudo-spin-valve, where the magnetization directions of the SM and HM are denoted with different arrows. (Data are from Ref. [140]) 6
- Fig. 2-2 Schematic model for spin dependent tunneling. (Data are from Ref. [140]) 11
- Fig. 2-3 Schematic energy band structure for a half metal. (Data are from Ref. [140]) 11
- Fig. 2-4 Spin polarization of tunneling electrons vs. the magnetic moment μof the electrode. (Data are from Ref. [141]) 12
- Fig. 2-5 TMR and μ^2 as function of the composition of Fe-Co alloy electrodes used for the junctions. (Data are from Ref. [141]) 12
- Fig. 2-6 AES depth profiles for (a) IrMn-CoFe-AlOx, (b) IrMn-Ta-CoFe-AlOx, (c) IrMn-CoFe-Ta-AlOx film stacks after annealing at 300°C, and (d) Mn profiles for the three multilayers after annealing at 300°C. (Data are from Ref. [68]) 20
- Fig. 2-7 Annealing temperature dependence of TMR ratio and RA for tunnel junctions with (a) CoFe and (b) CoFe/CoFeOx/CoFe pinned layers. \bullet (\circ), \blacktriangle (\triangle), and \blacksquare (\Box) represent the data for the junctions prepared under the same conditions, and solid and dashed lines indicate TMR ratio and RA, respectively. (Data are from Ref. [69]) 21
- Fig. 2-8 Volume compressions for Os, Ir, Re, Ru, W, and C. Error bars are shown for Os, Ir, and Ru. (Data are from Ref. [90]) 29
- Fig. 2-9 Backscattering spectra for osmium samples heat treated for one hour at 730, 740, and 750 $^{\circ}$ C, respectively, showing the transition from $Os₂Si₃$ to OsSi_2 . (Data are from Ref. [95]) 29
- Fig. 2-10 The indexed pattern of overlapping (040) OsSi₂ // (220) Si and [102] OsSi2 // [111] Si, after 200-1000°C, two-step annealing. (Data are from Ref. [96]) 30
- Fig. 2-11 Coercivity H_c and coercive squareness S^{*} before (\circ :H_c, \Box : S^{*}) and after (\bullet) :H_c, \blacksquare : S^{*}) magnetic annealing as a function of Os constant. (Data are from Ref. [97]) 30
- Fig. 2-12 Relation between Os content and the magnetic properties of γ –Fe₂O₃ thin films. The reduction temperatures of pure and Os- added films were 300 and 250°C, respectively. (Data are from Ref. [98]) 31
- Fig.2-13 Cross-sectional SEM images of Cu electrodeposited directly in trenches 31

of various aspect ratios. The Os barrier upon which the Cu was electrodeposited is visible as a bright layer beneath the Cu. (Images are from Ref. [14])

- Fig. 3-1 Image of the magnetron sputtering setup. This system has six sputtering guns with different materials, and the base pressure is below 5×10^{-9} Torr. 34
- Fig. 3-2 Image of the E-gun evaporation system. This setup includes 12 crucibles which can hold 12 different materials, and the best pressure is 5×10^{-8} Torr. 34
- Fig. 3-3 Schematic illustration of the epitaxial relationships between Cu and Si (001). The epitaxial relationships are: Cu (001) // Si (001) and Cu $[010]$ // Si [110]. 36
- Fig. 3-4 The XRD pattern of Cu grown on H-Si (100) by MMES method. The Cu (002) peak can be observed clearly even the Cu file was only 30 nm. (Data are from [142]) 36
- Fig. 3-5 Image of the field annealing setup. This system has an electromagnet and a vacuum anneal chamber, and the working pressure is 1×10^{-3} Torr. 38
- Fig. 3-6 Schematic illustration of the MOKE setup. 41
- Fig. 3-7 The Auger electron spectrum on the surface in the CoFe layer. The main peaks of Co, Mn, and Fe were overlapped in this energy range. 42
- Fig. 4-1 The XRD patterns of the MTJ with 15 nm PtMn before and after annealing at 300°C for 1 hour. 47
- Fig. 4-2 The (a) peak-positions and the (b) FWHM of each peaks of PtMn and CoFe are functions of PtMn thickness and annealing treatment. 47
- Fig. 4-3 The XRD intensity for PtMn, CoFe and NiFe as a function of diffraction angles for samples (with $d = 15$ nm) without annealing and annealing at 400°C for 10 minutes. 48
- Fig. 4-4 The PtMn peak position of MTJ samples with different PtMn thickness after different 400°C annealing times. 48
- Fig. 4-5 The peak intensities $((a), (b))$, the peak-positions $((c), (d))$, and the FWHM of peaks of PtMn and CoFe ((f), (g)) for samples with d varied from 8 to 20 nm after 400°C annealing for different annealing time. 49
- Fig. 4-6 XRD intensity and FWHM of PtMn peak for samples with d varied from 8 to 20 nm and annealing at 400°C for 10 minutes and 1 hour. 50
- Fig. 4-7 (a) The PtMn base MTJ showed stronger H_{ex} after field annealing(\Box) (T_a $= 275^{\circ}$ C, H_a = 7,500 Oe) near 4,300 Oe instead of the weaker H_{ex} after annealing without field (\bullet) ; (b) H_{ex} induced by PtMn was as a function 51

of PtMn thickness (d).

- Fig. 4-8 (a) The MR loop of the PtMn based MTJ after patterning showed a MR ratio near 30 %; (b) Normalized MR ratio versus post-annealing time, T_{PA} , for different annealing temperature. 51
- Fig. 4-9 The 400°C annealed MOKE measurements of (a) CoFe/Ru 0.8/CoFe/PtMn and (b) CoFe/Os 0.8/CoFe/PtMn, respectively. 58
- Fig. 4-10 The H_{ex} of Ru and Os base SAF film are as functions of the annealing temperature. 58
- Fig. 4-11 The AES depth profiles of (a) Ru base SAF, (b) Os base SAF, and (c) Ru base SAF with thick NOL after 400°C annealing. 59
- Fig. 4-12 The MOKE measurements of CoFe/Os (d)/OsMn. (a) shows that 2 nm Os can be retained the CoFe hysteresis loop as the same with as-deposited even after 400°C annealing. (b) indicates that the CoFe hysteresis loop can be retained can be retained after 400°C annealing even the inserted Os layer was as thin as 0.5 nm. 61
- Fig. 4-13 AES-depth profiles for the CoFe/Os (d nm)/OsMn multilayer before (a), (c) and after (b), (d) annealed at 300° C ((a), (b): d=0; (c), (d): d=1). 62
- Fig. 4-14 The AES depth profiles of Ta/CoFe/OsMn (a) without and (b) with 1 nm Os interlayer as a diffusion barrier after 400°C annealing. 63
- Fig. 4-15 The temperature dependence of H_C (\blacksquare and \Box) and S (\bullet and \circ) in the CoFe/Os (d nm)/OsMn multilayer, which indicated by $d = 0$ (dark symbol) and $d = 2$ (open symbol). The annealing conditions are 30 minutes at 1 kOe external field. 63
- Fig. 4-16 The Os barrier thickness dependence of: (a) the magnetization curve squareness and (b) the coercivity field in the Ta/CoFe/Os(d nm)/MnOs before and after 400°C annealing. (c) is the Os interlayer thickness dependence of the squareness and the normalized H_c after 400 $^{\circ}$ C annealing. 64
- Fig. 4-17 The VSM measurement of the Ta/CoFe/IrMn/CoFe/SiO₂ multilayer (a) without and (b) with a 0.3 nm Os barrier inserted in the upper part of the CoFe/IrMn interface. The H_{ex} of the annealed sample with the 0.3 nm Os barrier (\circ) was larger than that of the as-deposited state (\blacksquare). 65
- Fig. 4-18 An illustration of the possible diffusion model of Mn atoms interdiffusion in the CoFe/IrMn interface. 65
- Fig. 4-19 The XRD measurements of the Ta/CoFe/IrMn/Os/Ta/SiO₂ multilayer: (a) the influence of the IrMn exchange coupled CoFe films with and without the Os buffer and (b) enhancement of the diffraction peaks varied as increasing of the Os thickness. 75
- Fig. 4-20 The diffraction peak intensities of the IrMn (111)/Os (0002) and CoFe (111) , and H_{ex} varied as a function of the Os buffer thickness. 76
- Fig. 4-21 (a) XRD patterns of the evidence that the Os (0002) can provide a suitable surface mesh to grow fcc (111) orientation. (b) XRD pattern of CoFe/IrMn grown on Cu/H-Si (100) and Cu/H-Si (111) with and without Os buffer layer. 77
- Fig. 4-22 The $I_{irMn (111)}$ on Si (100) and Si (111) and the relative intensity of I_{irMn} (111) $\frac{1}{\text{Tr}}\text{Mn}$ (200) were a function of t_h. 78
- Fig. 4-23 The M-H loop of as deposited (a) and 200°C annealed (b) of CoFe/IrMn/Os30/Cu on both H-Si (100) and H-Si (111) substrates with Os buffer layer. 78
- Fig. 4-24 The Hex of the textured and poly-crystalline (poly) samples is as a function of T_a . The textured CoFe/IrMn film showed better thermal stability than the poly sample. The 50°C and 75°C of improvements on the temperature of obtaining the $H_{ex, max}$ and the H_{ex} disappearing were found clearly. 79
- Fig. 4-25 The XRD results of the textured IrMn film grown on Os/Cu buffer layer as Ta increased and only a small destruction of IrMn film structure is found when $T_a = 400^{\circ}C = 15$ 80
- Fig. 4-26 The XRD results of the textured CoFe/IrMn with and without the Os insertion layer in the interface. Such a thin inserted Os layer does not affect the film structure. 81
- Fig. 4-27 The H_{ex} of the textured samples with different d are as a function of T_a . The 0.3 nm Os inserted textured CoFe/IrMn film showed better thermal stability than the textured one without d. It is clearly found that the 50 \degree C improvement on the temperature, at which the H_{ex} disappearing. 82
- Fig. 4-28 The H_{ex} of the textured CoFe/Os (d)/ IrMn samples with $d = 0.3$ nm and $d = 1.0$ nm showed similar temperature dependence. 83
- Fig. 4-29 The H_{ex} of the textured sample is as a function of d. A thin Os barrier in the interface of the CoFe/IrMn made it more stable at high temperature. When $d > 0$, the all samples with $T_a = 300^{\circ}$ C showed larger H_{ex} than that of as-deposited state, while the H_{ex} of the sample without $d = 0$ nm degraded sharply. 84
- Fig. 4-30 The Hysteresis loop of the CoFe/Os 0.1/IrMn textured sample. The whole magnetic behavior was almost the same before and after 300°C annealing. Only half reducing of magnetic moments and a little rising of Hex were found. 84
- Fig. 4-31 The X-ray diffraction patterns of as-deposited 30 nm Cu film, and 30 92

nm Os films with and without 30 nm Cu buffer layer on Si(100), respectively. Clear Os (0002) peak and weak Os (1011) peak were observed. The inserted picture shows that the intensity of the Os (0002) was strongly dependent on the thickness of Os layer.

- Fig. 4-32 (a) the cross section TEM image of the Ta/ Os $30/$ Cu $20/$ Si(100). Many areas show very good layer by layer microstructures in the (b) interface between Cu and Os and (c) Os layer. 93
- Fig. 4-33 The X-ray diffraction patterns of the Os (0002) peak intensities for samples with the thickness of Cu buffer layer varied from 1 to 30 nm. 94
- Fig. 4-34 (a) the X-ray φ scans of the Os $\{1011\}$ of the Os on Cu (002)/ Si(100). (b) is a schematic illustration of the epitaxial relationships between Os (0002) and Cu (002) . The relationships are: Cu $(002)/\sqrt{OS(0002)}$, Cu[110]//Os[1120], Cu[110]//Os[2110] in "A" grain, and Cu(002)//Os(0002), Cu[110]//Os[1120], Cu[110]//Os[1230] in "B" grain. 95
- Fig. 4-35 (a) is the cross section TEM image of the Ta/ Os 30/ Cu 10/ Si (111), and (b) is the high magnification view of the interface between Cu and Os layers; while the white dash line roughly presents the non-smooth interface and the white arrows indicate the different growth direction of the Os (0.002) near the interface. (c) is the X-ray ω scans of the Os {1011} of the Ta/ Os 30/ Cu 10/ Si (111). 96
- Fig. 4-36 (a) The XRD pattern of Os on H-Si (111) with Pd buffer layer. The inst shows the XRD φ scan results. (b) Some dislocations were found in the cross sectional TEM image between the interface of Pd and Os. 97
- Fig. 4-37 The XRD patterns of Os on (a) Au and (b) Ag buffer layer on Si (111) showed they were both epitaxial growth. The inst in both figures shows the $XRD \varphi$ scan results, respectively. 98
- Fig. 4-38 (a) The XRD pattern of Os on H-Si (111) with buffer layer. The XRD φ scan results of Au (the inset in (a)) and (b) Ag both indicated the Os film and the buffer layer were epitaxial growth. 99
- Fig. 4-39 (a) The TEM cross sectional images of Os/Cu/Au/H-Si (111) shows the 100 films growth is closed to epitaxial growth. (b) is the high magnification image of Os/Cu interface and the uniform atomic arrangement can be found. The inset presents the TEM electron diffraction pattern of Os/Cu interface.
- Fig. 5-1 Schematic illustration of the Os uses on combining ULSI processes 104 with MTJ manufacturing.