

摻雜不同濃度碳的二氧化鈦薄膜之電子結構與磁性研究

研究生：郭哲余

指導教授：莊振益 教授

國立交通大學 電子物理學系碩士班

中文摘要

本研究中，我們利用固態燒結法製備摻雜碳的二氧化鈦粉末，再使用油壓機和箱形爐來對粉末加壓和加熱，使其成為塊材。接著我們使用脈衝雷射鍍膜系統進行鍍膜，並在一系列成長條件下探討碳摻雜對二氧化鈦磁性造成的效應和機制。我們發現摻雜碳的二氧化鈦有明顯的磁滯曲線，顯示碳摻雜確實會形成室溫鐵磁性。本論文藉由 C-1s 和 Ti-2p 之 XPS 量測，發現薄膜中有鈦和碳的鍵結與氧空缺，顯示摻碳二氧化鈦的鐵磁性來源，是由氧空缺與雜質間相互作用所產生。從 O-1s 的 XPS 也可以看出，摻雜碳可使氧空缺變多，此可能進而產生更多電子。本實驗也發現隨著碳的摻雜濃度增加，鐵磁性並未維持一直增加的趨勢，甚至反而減弱材料的室溫鐵磁性，本論文亦將對此現象，提出初步的解釋。

Electronic structure and magnetism in TiO₂ thin films doped with different concentrations

Student : Che-Yu Kuo

Adviser : Prof. Jenh-Yih Juang

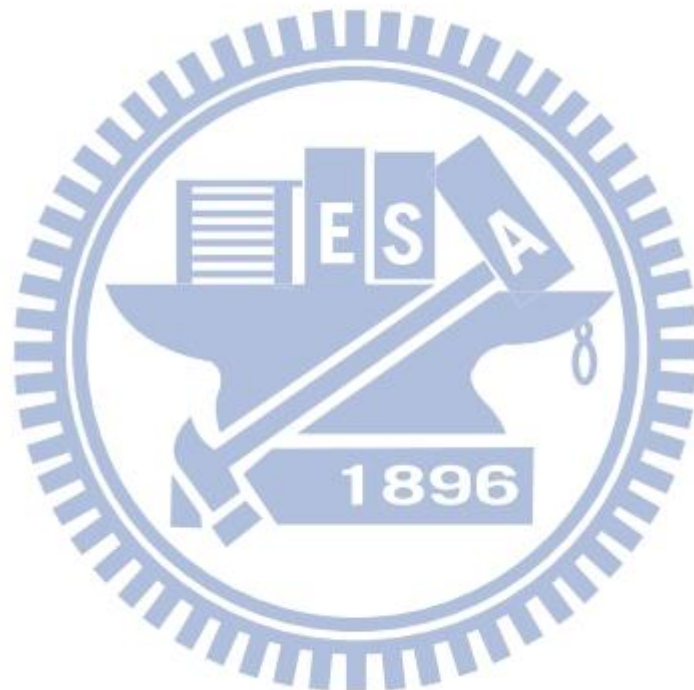
Department of Electrophysics
National Chiao Tung University

Abstract

Carbon-doped titanium dioxide powders was prepared by solid state sintering at 1200 °C for 24hrs to produce TiO₂ bulks with different carbon doping concentrations. The obtained TiO₂ bulks were then used to deposit TiO₂ thin films by pulsed laser deposition. The effects of carbon doping was investigated via a series of films obtained at various deposition conditions. The results indicate that the carbon-doped titanium dioxide evidently exhibit significant magnetization hysteresis at room temperature, indicating the realization of room-temperature ferromagnetism (RTFM).

Further X-ray photoelectron spectroscopy (XPS) analysis on C-1s, O-1s, and Ti-2p electronic states showed the existence of Ti-C bonding and significant

amount of oxygen vacancies. These results lend support to the p-p interaction, induced ferromagnetism in these oxides. The observed RTFM, however, did not increase with increasing doping concentration of carbon, presumably due to the excessive free carbon-induced diamagnetism.



Acknowledgement

這本論文的完成，真的很感謝大家。首先在碩士生涯要感謝我的指導教授莊振益老師，老師總是對學生的想法和實驗表示支持，讓我在光譜，磁性量測，同步輻射中心的實驗可以順利進行，最後的吸收光譜實驗分析更是給了我很多的幫助。此外也要感謝實驗室的學長們，謝謝您們當初在我碩一時帶我做實驗，教導我實驗的操作技巧，給了我論文實驗的架構參考方向。還記得當初第一次 meeting 完還甚麼都不懂的多鐵材料，還記得當初還想要研究過的龐磁阻，還記得當初對其懵懵懂懂的光觸媒，想不到這也變成我最後的研究材料。感謝韋呈學長在磁性量測上的幫忙，常常在數據的分析上有些問題學長都能給我些實驗的方向和意見；感謝培源學長的照顧，還會建議我買甚麼電腦，有哪些助教機會可以接等等；感謝皓葦學長在鍍膜的實驗上給了我很多建議，在電子能譜儀的數據分析上也給了我很多幫助；感謝家宏學長、宗翰學長、家彬學長、彥智學長、俊宇學長教我操作儀器做實驗，特別要感謝家彬學長給了我很多實驗研究的方向，和學長將當初實驗的瓶頸和注意事項交给了我，對我的實驗方向的建構有了很大的幫助；還有碩二時才進來實驗室的學弟妹們，博班學長姐們，也給了我很多幫助和給實驗室帶來了朝氣，我口試時也幫了我很多忙，由衷的感謝你們大家，謝謝大家對我的包容和關心。

然後我想把這份喜悅分享給我的家人，也謝謝您們支持我，總是吩咐我不要為了薪水接太多工作，不要為了外務而太勞累，是我無後顧之憂讀書做實驗的最大動力，會聽我的想法給我建議支持我想做的事，這真的就是我進步的最大動力。當我不想選擇研發替代役這條路時也支持我選擇另外一條軍旅生涯，這邊也可以很高興地在碩士生涯聽到母親退休不在那麼勞累的消息。希望爸媽們身體健康，這就是我在外打拼最安心的消息了。

最後引用陳之蕃的一句話:要感謝的人太多了，那就謝天吧。願大家將來都能事事順心，平平安安，希望這股緣份激起的漣漪，將來能在重溫邂逅。



Contents

Abstract (in Chinese)	i
Abstract (in English)	ii
Acknowledgement	iv
Contents	vi
List of Figures	viii
Chapter 1 Introduction	1
1-1 Magnetic materials and semiconductors	1
1-2 Diluted Magnetic Semiconductors (DMSs)	3
1-2.1: What's DMS	3
1-2.2: Types of DMSs	5
1-2.3: The development of DMSs	8
1-2.4: Why DMSs are so important?	14
1-3 Titanium dioxide	15
1-3.1: Photocatalyst	15
1-3.2: Literature review of TiO ₂	16
1-3.3: The crystal structure of titanium dioxide	23
1-3.4: TiO ₂ -based materials	25
1-3.5: 2p-light element doped DMSs	26
1-4 Motivation	28
Chapter 2 Background	29
2-1 Brief introduction to magnetism	29
2-2 Types of magnetism	32
2-3 The mechanism and source of magnetism in DMSs	38
2-3.1: Bound magnetic polaron (BMP)	42
2-3.2: Mechanism of exchange interaction	44

Chapter 3	Experiments and Instruments	48
3-1	Sample preparation	48
	3-1.1: Target fabrication	48
	3-1.2: Pulsed laser deposition (PLD)	49
3-2	Structure analysis by XRD	50
3-3	Analysis of magnetism	51
	3-3.1: Introduction of the SQUID	51
	3-3.2: The principle of Josephson junctions	53
3-4	Surface electronic structure analysis	54
	3-4.1: What's X-ray Photoelectron Spectroscopy?	54
	3-4.2: Chemical State Identification	55
3-5	X-ray absorption near edge structure (XANES)	57
Chapter 4	Results and discussion	60
4-1	The characteristics of carbon-doped TiO ₂ powders	60
	4-1.1: Structure Analysis of powders by X ray Diffraction(XRD)	60
	4-1.2: Magnetic analysis of powders by SQUID	61
4-2	The characteristics of carbon-doped TiO ₂ thin films	64
	4-2.1: Structure analysis of thin films by X-ray Diffraction	64
	4-2.2: Magnetic analysis of thin films by SQUID	66
4-3	Surface electronic structure analysis by XPS	67
4-4	Diamagnetic effect caused by excessive carbon	72
4-5	XANES analysis	74

List of Figures

Fig. 1.1	Schematic illustration of (A) magnetic semiconductor (B) diluted magnetic semiconductor; and (C) nonmagnetic semiconductor.	4
Fig. 1.2	(a) Comparisons of II-VI DMSs, III-V DMSs, and oxides. (b) Curie Temperature for various p-type semiconductors (c) Bandgap versus lattice constant at room temperature for common elemental and binary compound semiconductors.	7 9 10 10
Fig. 1.3	Hall resistivity as a function of applied magnetic field measured at different temperatures for (Ga, Mn)N.	11
Fig. 1.4	(a) The M-T curve of Mn-doped ratio of 9% by Sonoda. (b) The M-T curves of Mn-doped ratio of A (12%) and B (1.4%) by Hashimo.	12
Fig. 1.5	Zn _{1-x} Co _x O of (a) M-T Curves (b) M-H Curves.	13
Fig. 1.6	M-H curves of sintered ZnMnO.	14
Fig. 1.7	Schematics showing the characteristics and applications of TiO ₂ .	15
Fig. 1.8	By OPA-MBE growth of single crystal Co _x Ti _(1-x) O ₂ film of the RHEED (a and d), SEM images (b and e) and Auger intensity maps (c and f).	17
Fig. 1.9	The M-T (ZFC-FC) curves of Co _x Ti _(1-x) O ₂ thin films with 0.01 ≤ x ≤ 0.12.	18
Fig. 1.10	(a) SEM image of Ti _{0.95} V _{0.05} O ₂ growth at 700°C. (b) M-T curves of Ti _{0.95} V _{0.05} O ₂ at different growth temperatures	20
Fig. 1.11	Structures of anatase and rutile phase TiO ₂ .	24
Fig. 2.1	The g value of various magnetic materials.	31
Fig. 2.2	The schematic illustration of paramagnetism.	32
Fig. 2.3	χ ⁻¹ -T curve of Langevin paramagnetism.	32
Fig. 2.4	Characteristic in magnetic susceptibilities of diamagnetism and paramagnetism.	33
Fig. 2.5	Hysteresis curve of ferromagnetic materials.	34
Fig. 2.6	(a) Diamagnetism (b) Paramagnetism (c) Ferromagnetism.	35

Fig. 2.7	Ordered arrangements in electron spins.	36
Fig. 2.8	Ferrimagnetism	37
Fig. 2.9	Ordering of magnetic dipoles in a various of magnetic materials	37
Fig. 2.10	The model of localized carrier theory.	40
Fig. 2.11	The model of itinerant carrier theory.	41
Fig. 2.12	BMP Model	43
Fig. 2.13	Schematic that depicts the hoping processes in double exchange	45
Fig. 2.14	Schematics depicting the hopping processes in super exchange and double exchange.	46
Fig. 2.15	Schematics illustrating (a) direct exchange (b) super exchange (c) indirect exchange	47
Fig. 3.1	Illustration of XRD process.	51
Fig. 3.2	Schematic illustration of SQUID.	52
Fig. 3.3	Josephson junctions	53
Fig. 3.4	Josephson Circuit	53
Fig. 3.5	X-ray Photoelectron Spectroscopy (XPS).	55
Fig. 3.6	Schematic illustration of XANES.	58
Fig. 4.1	The XRD of initial three kinds of powders.	61
Fig. 4.2	The M-H curves of the three kinds of powders.	62
Fig. 4.3	(a) XRD of pure TiO ₂ thin film at 400° C and 0.2torr. (b) XRD of 2%C-doped TiO ₂ thin film. (c) XRD of 5%C-doped TiO ₂ thin film. (d)The comparison of XRD of 5%C-doped and 2%C-doped TiO ₂ thin films.	64 65 65
Fig. 4.4	The M-H curves of the three kinds of thin films	66
Fig. 4.5	XPS of Ti 2p (Titanium dioxide with 0% carbon).	68
Fig. 4.6	XPS of Ti 2p (Titanium dioxide with 2% carbon).	68

Fig. 4.7	XPS of Ti 2p (Titanium dioxide with 5% carbon).	69
Fig. 4.8	XPS of C 1s (Titanium dioxide with 0% carbon).	69
Fig. 4.9	XPS of C 1s (Titanium dioxide with 2% carbon).	70
Fig. 4.10	XPS of C 1s (Titanium dioxide with 5% carbon).	70
Fig. 4.11	XPS of O 1s (Titanium dioxide with 0% carbon).	71
Fig. 4.12	XPS of O 1s (Titanium dioxide with 2% carbon).	71
Fig. 4.13	XPS of O 1s (Titanium dioxide with 5% carbon).	71
Fig. 4.14	Analysis of excessive magnetic moment.	72
Fig. 4.15	The Ti L-edge XANES.	74

