出國報告（出國類別：開會）

參加2019年第46屆國際冶金鍍膜與薄膜技術國際研討會

服務機關： 核能研究所
姓名職稱： 陳柏聞 副研究員
派赴國家/地區：美國/加州聖地牙哥
出國期間： 108年5月18日~108年5月26日
報告日期： 108年6月28日

摘 要

2109 年第 46 屆冶金鍍膜與薄膜技術國際研討會(46th International Conference on Metallurgical Coatings and Thin Films, ICMCTF2019)於 5 月 19 日至 24 日在美國加州聖地牙哥 Town and Country Resort Hotel 舉辦，此研討為國際最大規模的鍍膜研討會。參加本次研討會旨在配合本所電漿計畫執行，以瞭解真空鍍膜技術及設備之最新發展趨勢，包括高功率磁控脈衝電漿源 (High Power Impulse Magnetron Sputtering, HIPIMS) 鍍膜技術應用於石墨烯鋰電池及燃料電池、過濾式陰極電弧 (Filter Cathodic Arc Deposition, FCVA) 技術應用於氮化物薄膜與薄膜型氣體感測器等領域研究。特別是大面積電弧電漿鍍膜產業應用之相關技術，可作為未來主要的參考依據。

作者參加本次研討會以口頭方式發表本所電弧電漿鍍膜技術應用於電致變色元件研發成果，本發表技術具低成本、快速沉積鍍膜等優點，未來可導入高單價電致變色元件市場，會場中吸引多方專家關注，更增加本所國際知名度。作者榮幸能與參加此次多領域之國際著名專家學者深入討論，除讓研究思維更加廣闊外，且認識更多專家學者與吸收新知，掌握國際著名相關實驗室研究發展方向，可藉機創造更多的國際合作空間，掌握先機。

圖目錄

目　　次

一、目　的

2109 年第 46 屆冶金鍍膜與薄膜技術國際研討會(46th International Conference on Metallurgical Coatings and Thin Films, ICMCTF2019)含七大主題及鍍膜設備產品展，主題細分為: 1、高溫鍍膜應用(Coating for Use at High Temperatures); 2、硬薄鍍膜技術(Hard Coatings and Vapor Deposition Technologies); 3、多功能材料及元件製造技術(Fundamentals and Technology of Multifunctional Materials and Devices); 4、鍍膜技術應用於生醫與生物體開發(Coatings for Biomedical and Healthcare Applications); 5、表面鍍膜之耐磨耗與機械性質研究(Tribology and Mechanical Behavior of Coatings and Engineered Surfaces); 6、表面工程技術(Surface Engineering - Applied Research and Industrial Applications); 7、鍍膜應用與設備展覽會(Exhibition Keynote Lecture) 等領域。

參與本次研討會對未來研究方向提供啟發性的想法，尤其奈米複合材料及多層超晶格鍍膜兩項重要技術為未來發展上努力重點，亦可作為後續本組技術應用開發及未來計畫擬定與執行之參考。作者參加該研討會並發表電弧電漿源應用於互補式電致變色元件論文，除能彰顯本所於低成本電漿鍍製薄膜技術領域外，並期望藉由發表論文與專者討論過程中瞭解國際間研發現況，探求最新技術可行性，並強化合作關係並增益現有研發能量，期能加速本所在電漿製程設備產業化之時程。

二、過　程

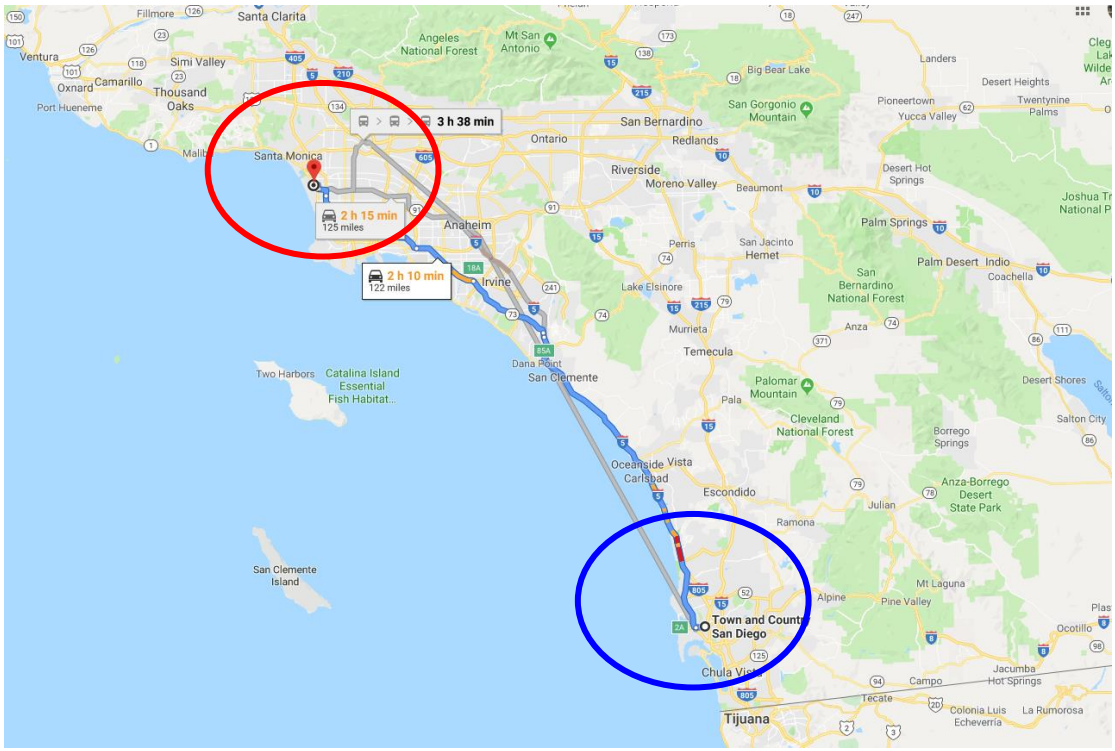
本次公差之行程如下：

5 月 18 日 (六)　晚上 19 時 20 分自桃園國際機場出發，於當地時間 5 月 18 日 16 時 20 分抵達洛杉磯國際機場。從機場附近租車前往聖地牙哥城鄉旅館(Town and Country Resort Hotel)會議地點，並於 21:30 到達飯店辦理入住事宜。本次研討會會場所在地，如圖 1。

5 月 19 日 (日) 於大會會場辦理會議報到與註冊程序:參加 ICMCTF 國際研討會、蒐集研發資料並參加大會主辦之短期課程 (Short Courses): NANOMECHANICS AND TRIBOLOGY OF THIN FILMS AND COATINGS 課程。

5 月 20 日 (一) ~5 月 24 日 (五) 參加 ICMCTF2019 國際研討會蒐集研發資料並發表電弧電漿源應用於互補式 WO_3/NiO 電致變色元件研發成果論文，於 5 月 22 日 (三) 上午 08 時 40 分~09 時 00 分，以口頭報告形式發表本組最新研發成果。

5 月 25日~26日 於當地時間 06時00分自飯店出發，前往洛杉磯國際機場。09時00分抵達洛杉磯國際機場，並於12時15分自美國加州洛杉磯國際機場前往桃園國際機場，抵達台灣時間為5月26日 (日) 17時30分，順利完成本次公差任務。



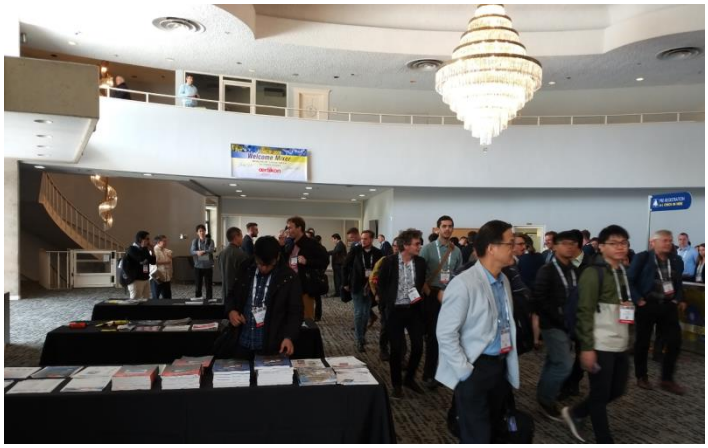


圖 1　Town and Country Resort Hotel 會議地點(上圖)及會議現場現況(下圖)

三、心　得

作者目前在核能研究所(以下簡稱本所)，從事電漿鍍膜技術開發。近期在開發低成本電弧電漿源應用於電致變色膜相關之研究工作有突破性的成果，並期望參加本次國際研討會能更瞭解目前世界上最新研發進展以及電漿技術在大面積電弧電漿鍍膜產業應用相關技術，故投稿參加「2019 年第46屆冶金鍍膜與薄膜技術國際研討會」。藉由參加該會議可搜集高功率電漿源技術應用於節能、儲能、新穎材料應用、綠色能源、環境電漿科學、電化學技術之應用發展現況，可作為未來計畫擬定與執行及往後計畫發展參考之依據。

美國真空協會 (American Vacuum Society, AVS) 是國際上最具知名的真空鍍膜學術研究組織，每年定期在加州聖地牙哥之城鄉旅館舉辦國際冶金鍍膜與薄膜技術(ICMCTF)研討會，會議場地報到指引(左上圖)、演講廳展示配置圖(右上圖)及大會演講現場(下圖)，如圖 2。今年大會為第46屆ICMCTF 2019，會期由5月19日至5月24日共6天，相關議程如圖 3。大會中投稿論文篇數超過850篇，其中48篇為受邀演講。來自20個以上國家，研究學者近380位參加以學術界為主，少數結合工業界先進就真空電漿鍍膜之理論與應用進行研討。會中以學術論文居多，主要探討PVD多層奈米功能性薄膜、二維材料成長機制、石墨烯鋰電池儲能元件及多層光學製程之開發與應用；而工業應用論文仍以傳統硬膜在工具、膜具、刀具、光學、機械、半導體與生醫等領組件應用為主，本次會議內容以演講為主，少數則以海報呈現。會議現場主要分為十個演講廳，如圖 4。唯一可惜的地方為在會場不能錄音及照相，如圖 5。在下面段落中所有圖片均由演講者簡報內容擷取出來，為作者會後向演講者索取簡報資料。

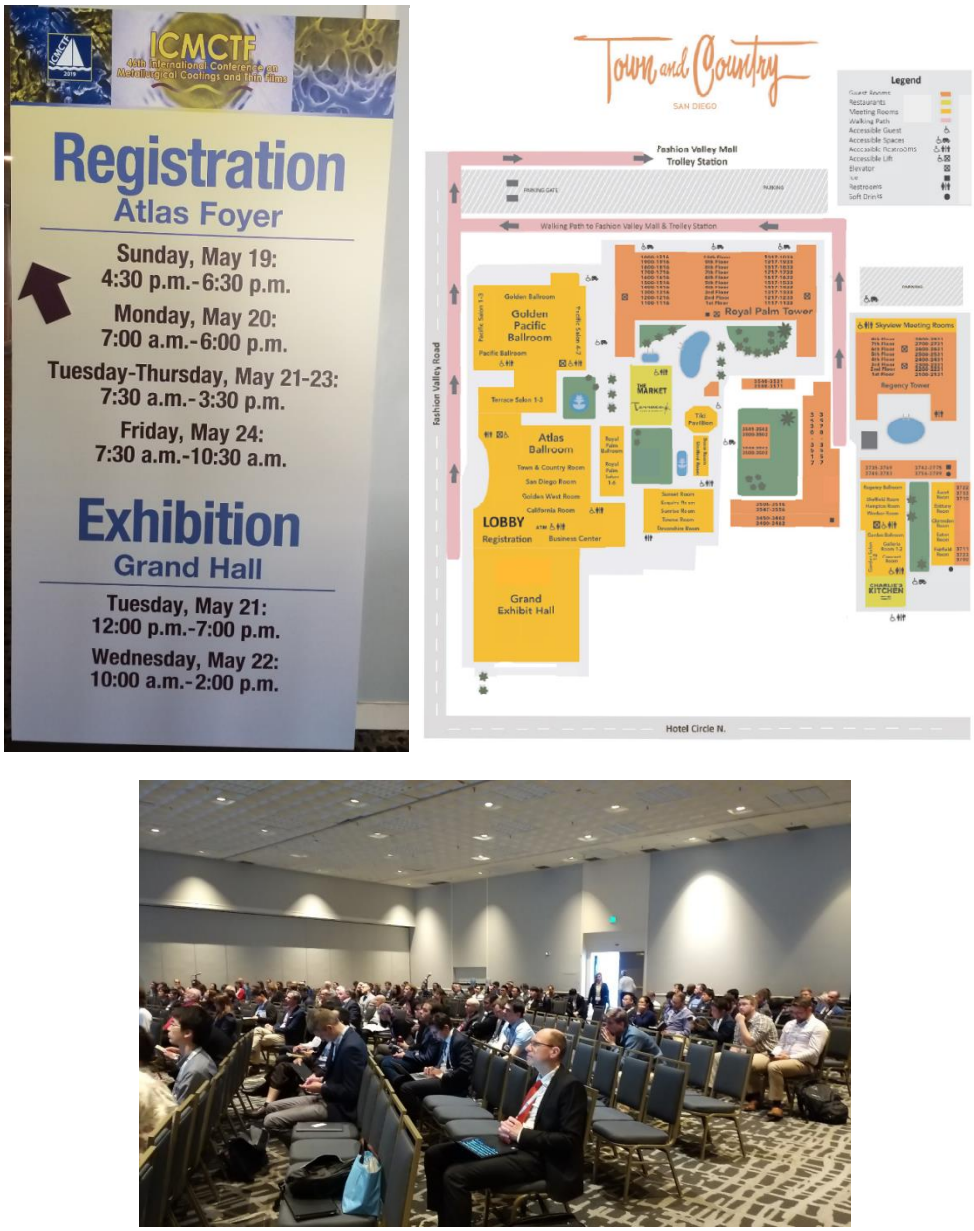


圖 2 會議場地報到指引(左上圖)、演講廳展示配置圖(右上圖)及大會演講現場(下圖)

2019 ICMCTF SCHEDULE OF EVENTS

DAY	TIME	EVENT	LOCATION
SUNDAY	7:30 am – 8:30 am	Short Course Registration	Atlas Foyer
	8:30 am – 4:30 pm	Short Course Program	Atlas Foyer
	4:30 pm – 6:30 pm	Conference Registration	Atlas Foyer
MONDAY	7:00 am – 6:00 pm	Conference Registration	Atlas Foyer
	7:30 am – 8:30 am	Short Course Registration	Atlas Foyer
	8:00 am – 9:45 am	***Plenary Session Lecture: Professor John Rogers*** *"Soft Electronics for the Human Body"*	**Town & Country Room**
	8:30 am – 4:30 pm	Short Course Program	Atlas Foyer
	10:00 am – 5:40 pm	Technical Sessions	See Program/Mobile App
	12:20 pm – 1:20 pm	***Focused Topic Session: Anton Paar*** *"Latest Developments in Advanced Mechanical Surface Characterization"*	Town & Country Room
	5:45 pm – 7:00 pm	**ICMCTF 2019 Welcome Mixer**	**Lion Fountain Courtyard**
TUESDAY	7:00 am – 8:00 am	***Focused Topic Session: Bruker*** *"Advanced Technologies for the In-Depth Characterization of Surfaces"*	Town & Country Room
	7:30 am – 8:30 am	Short Course Registration	Atlas Foyer
	7:30 am – 3:30 pm	Conference Registration	Atlas Foyer
	8:00 am – 5:40 pm	Technical Sessions	See Program/Mobile App
	8:30 am – 4:30 pm	Short Course Program	Atlas Foyer
	11:00 am – 12:00 pm	***Exhibition Keynote Lecture: Dr. Farwah Nahif*** *"Advanced Performance of Tools in Sheet-metal Forming-The Synergy of Surface Technology and Tooling Material Selection"*	**Town & Country Room**
	12:00 pm – 7:00 pm	**Exhibition Hall Opens Today**	**Grand Hall**
	12:00 pm – 1:40 pm	Light Lunch in Exhibit Hall (While Supplies Last)	Grand Hall
	3:20 pm – 4:00 pm	Break – Complimentary Refreshments in Exhibit Hall	Grand Hall
	5:30 pm – 7:00 pm	**Exhibition Reception**	**Grand Hall**
	7:00 pm – 8:00 pm	***Special Interest Talk: Grégory Abadias*** *"Advanced Monitoring of Thin Film Growth from Real-time Diagnostics"*	**Town & Country Room**
WEDNESDAY	7:30 am – 3:30 pm	Conference Registration	Atlas Foyer
	7:30 am – 8:30 am	Short Course Registration	Atlas Foyer
	8:00 am – 5:40 pm	Technical Sessions	See Program/Mobile App
	8:30 am – 4:30 pm	Short Course Program	Atlas Foyer
	10:00 am – 2:00 pm	Visit the Exhibition!	Grand Hall
	10:00 am – 11:00 am	Break – Complimentary Refreshments in Exhibit Hall	Grand Hall
	12:20 pm – 2:00 pm	Light Lunch in Exhibit Hall (While Supplies Last)	Grand Hall
	1:00 pm – 2:00 pm	***Special Interest Talk: Ivan Petrov*** *"Linking Intrinsic Plasma Characteristics to the Microstructure and Properties of Thin Films"*	**Town & Country Room**
	5:45 pm – 7:15 pm	**Awards Convocation: *Dr. Joe Greene*** *"Some Highlights from over Four Decades of Thin-film Science"*	**Town & Country Room**
	7:30 pm – 10:00 pm	Awards Buffet Reception	Golden Ballroom
THURSDAY	7:30 am – 3:30 pm	Conference Registration	Atlas Foyer
	7:30 am – 8:30 am	Short Course Registration	Atlas Foyer
	8:30 am – 4:30 pm	Short Course Program	Atlas Foyer
	8:00 am – 5:00 pm	Technical Sessions	See Program/Mobile App
	12:20 pm – 1:20 pm	**ICMCTF 2020 Information Session**	**California**
	12:20 pm – 1:20 pm	***Focused Topic Session: Elsevier*** *"The Art of Publishing"*	Golden West
	5:00 pm – 7:00 pm	**Poster Session (including 4 HDTV poster demonstrations)**	**Grand Hall**
	6:00 pm – 7:00 pm	**Poster Reception**	**Grand Hall**
FRIDAY	7:30 am – 10:30 am	Conference Registration	Atlas Foyer
	8:00 am – 12:00 pm	Technical Sessions	See Program/Mobile App
	12:00 pm – 1:00 pm	**Thank You, See You Next Year Party!**	**Lion Fountain Courtyard**

圖 3 國際冶金鍍膜與薄膜技術研討會議程表

Room /Time	Atlas Foyer	Town & Country	Grand Hall	California	Golden West	Pacific Salon 1	Pacific Salon 2	Pacific Salon 3	Pacific Salon 6-7	San Diego
Sun: am & pm	SC Reg: 7:30 - 8:30 am Conf. Registration: 4:30-6:30pm									
Mon: 8:00 am	SC Reg: 7:30-8:30 am Conf. Registration: 7:00 am – 6:00 pm	PLENARY: John Rogers 8:00–9:45 am								
Mon am: 10:00 am Start	Registration Continues	FTS: Anton Paar 12:20-1:20 pm		B3-1-MoM: Deposition Tech. & Applic. for Diamond-like Coatings I	B1-1-MoM: PVD Coatings and Technologies I	H2-1-MoM: Fatigue and Wear	D1-1-MoM: Surface Coating and Modification for Use in Biological Environments I	TS4-1-MoM: Thin Film Materials for Flexible Electronics		
Mon pm: 1:40 pm Start	Welcome Mixer 5:45-7:00 pm Lion Fountain Courtyard		Exhibit Staff Setup 3:00 pm	B3-2-MoA: Deposition Tech. & Applic. for Diamond-like Coatings II	B1-2-MoA: PVD Coatings and Technologies II	H2-2-MoA: Nanoscale Plasticity	D1-2-MoA: Surface Coating and Modification for Use in Biological Environments II	TS3+4-2-MoA: Surface Eng. for Lightweight Materials & TF Matls for Flexible Electronics		

圖 4 十大演講廳議題探討

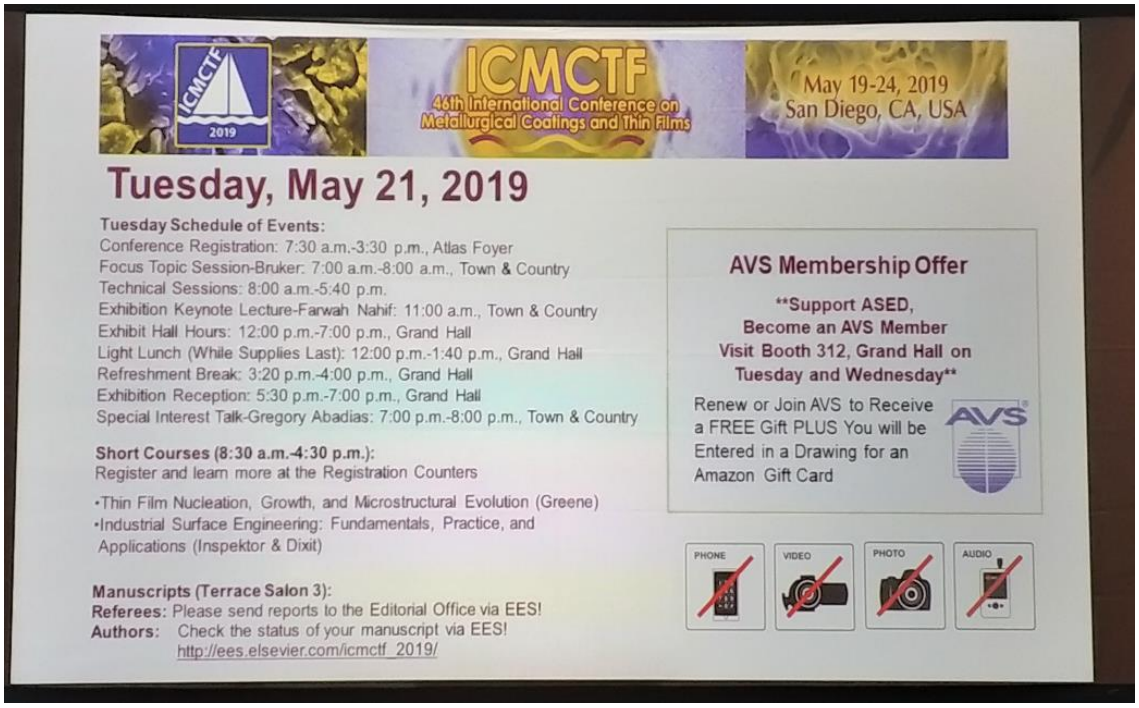


圖 5 會議大會規定不能使用手機、錄影及照相

本次國際研討會於5月20午7時開始接受註冊登記，緊接著在上午8時3舉辦開幕儀式，開始今日的講座，首先是兩場Plenary Lecture，大會Plenary Section Leture由 Prof. John Rogers開序，介紹軟性積體電路應用於人體(Soft Electronics for the Human Body)，Prof. John Rogers 於1995年在麻省理工學院獲得物理化學博士，他的研究旨在利用“軟”材料的特性，如聚合物，液晶和生物組織，以及它們與不同類型的微/納米材料的混合組合，開發新材料如誘導新的電子和光子響應， 並開發新的“軟平版印刷”用於圖案化。這項工作將基礎研

究與前瞻性工程努力相結合，納米光子結構，微流體裝置和微機電系統的軟材料。

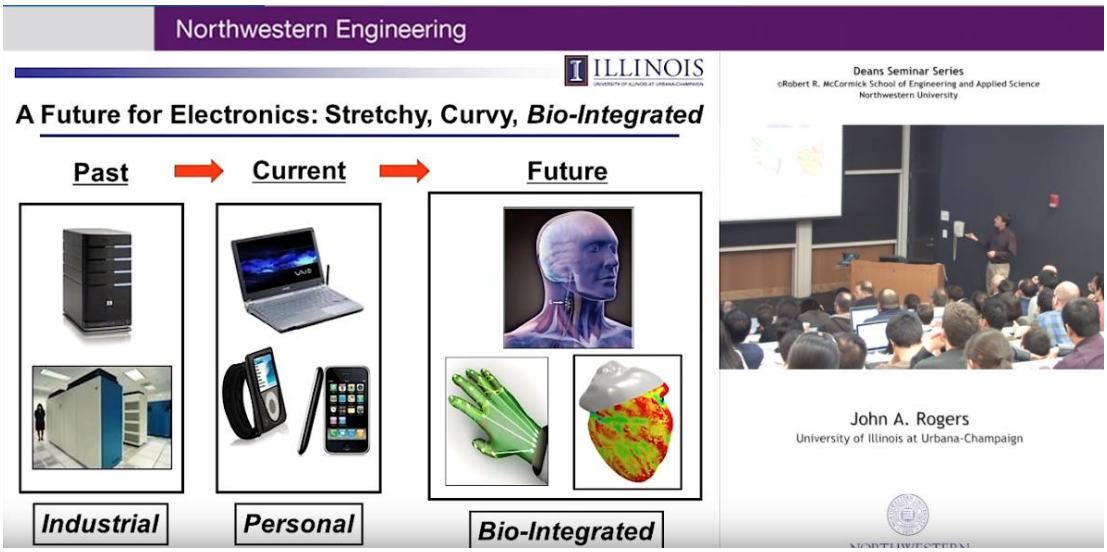


圖 6 介紹從過去大型電腦逐步到未來軟性電子商品客製化應用於生物整合系統

如圖 6 介紹未來軟性電子商品應用於生物整合系統。Prof. John Rogers 也介紹人類導入物聯網穿戴裝置後，如圖 7，系統可以明確知道病患現在的物理和生理狀況。無線感測器結合射頻(RF)電路板模組，可結合手機顯示功能傳感身體內有些許變化，會改變電壓與電流源讀值來判別是否有異。如果病人昏倒在地，身上的穿戴裝置會自動通知護理站，醫護人員就可以在第一時間趕到現場，提供緊急處理。隨著遠距醫療不斷發展，技術成熟的城市，已經大幅縮減病患與診所之間的距離問題。現在和未來都會快速發展的物聯網(IoT)醫療，則能在未來提供更精準的醫療服務，為未來醫療相當重要的發展方向。

另外，Prof. John Rogers 也介紹智慧家庭的物聯網架構來看，目的在於建構家庭控制與自動化，從防盜門禁鎖、中央恆溫空調、LED 燈調光器、監控器、感應器閘道等硬體設施。藉由網際網路傳達到雲端服務平台，使用者再藉由平板、智慧手機、智慧手錶，登入雲端服務商提供的服務入口網站，再來監看家裡的各種即時狀況，或控制家裡的各種家電，如圖 8。做為 IoT 物物相連，連線距離從 20cm 以內、0.4Mbps 到 1~10 公尺屬個人網路(PAN)的應用範疇或新興穿戴式裝置(Wearable Devices)新產品、新應用的殺戮戰場。於 2013 年推出搭配低功耗藍牙(BLE)系統單晶片的嵌入式無線網路連結裝置(WICED)平台，僅一支隨身碟大小，內建必要的通訊協定堆疊並提供 Wi-Fi、BLE 等無線連網能力與服務，如圖 9。其中，最關鍵零組件為 Transient Electronics 工藝，如薄膜電晶體結構及傳感連接器，如圖 10。未來可應用於人體穿戴型裝置，將感測器配戴在人體上，若人體活動及發生危險時，將訊號傳出，整合成新商機，在未來人工傳感測器必然很重要的研發市場。

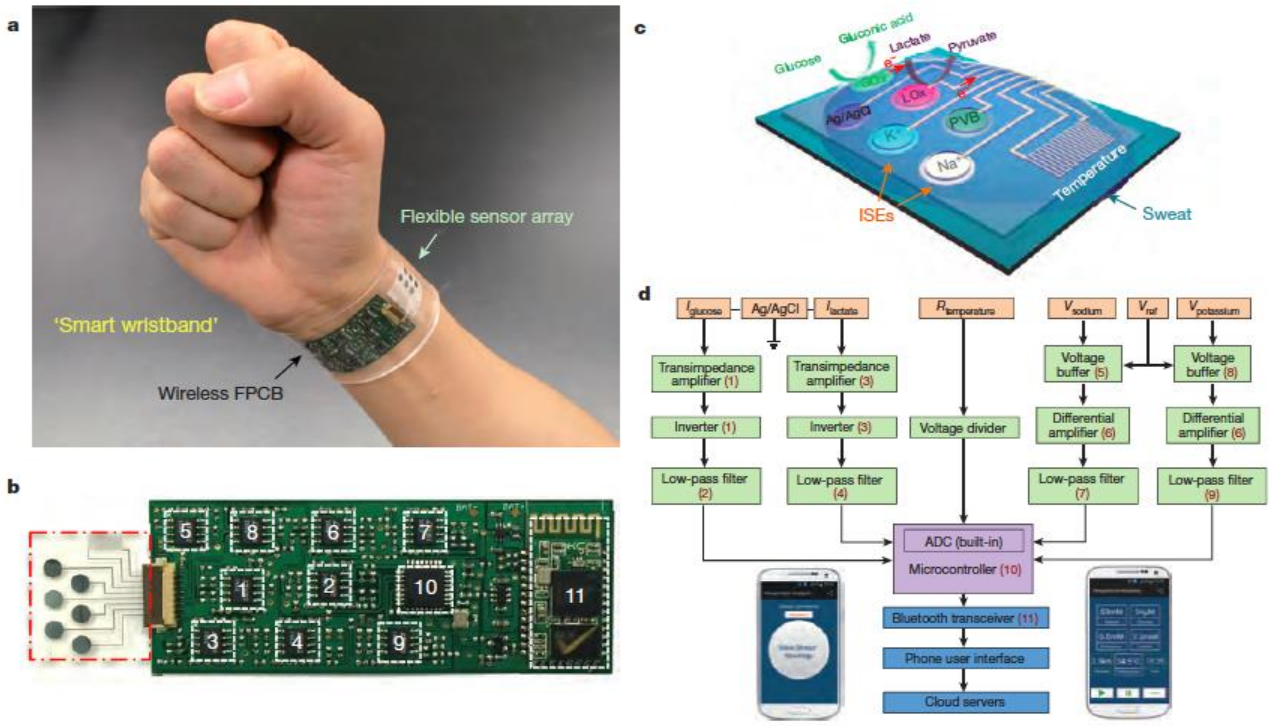


圖 7 無線感測器結合射頻(RF)電路板模組可預見，對未來人類有重大里程碑

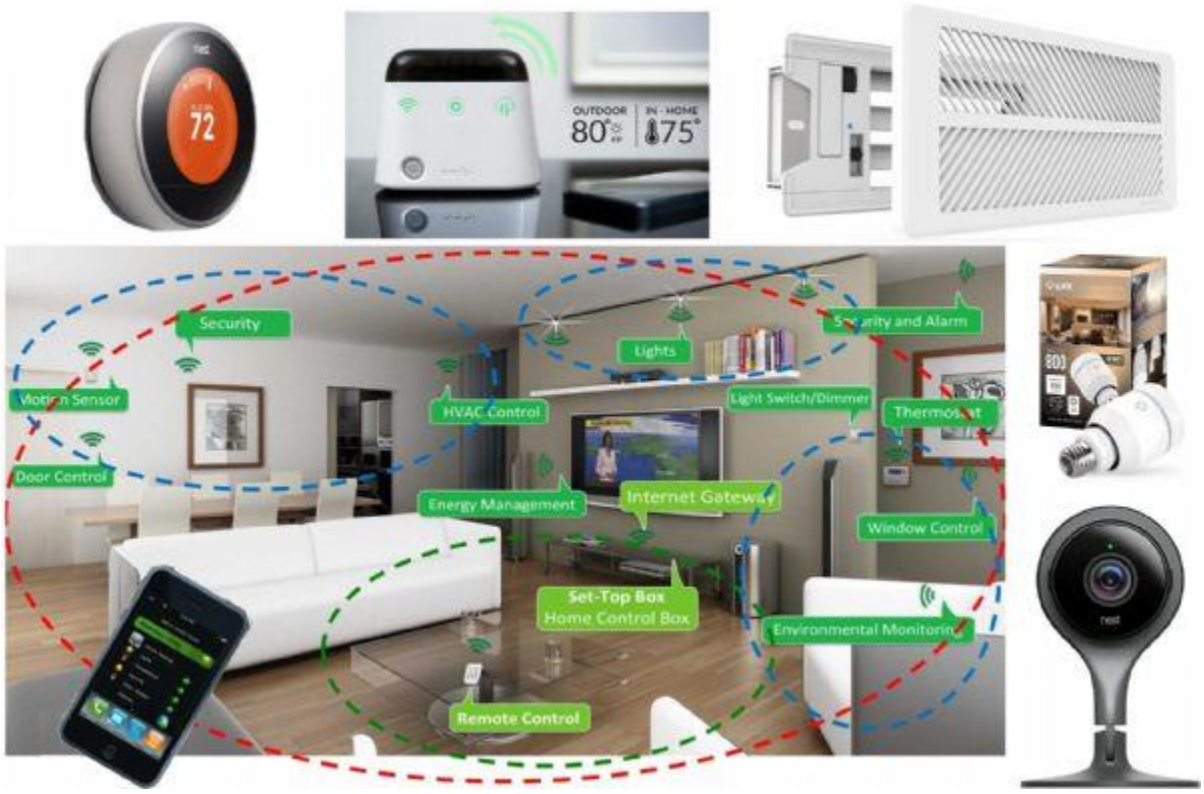


圖 8　介紹智慧家庭的物聯網架構

圖 9 搭配低功耗藍牙(BLE)系統單晶片的嵌入式無線網路連結裝置(WICED)平台

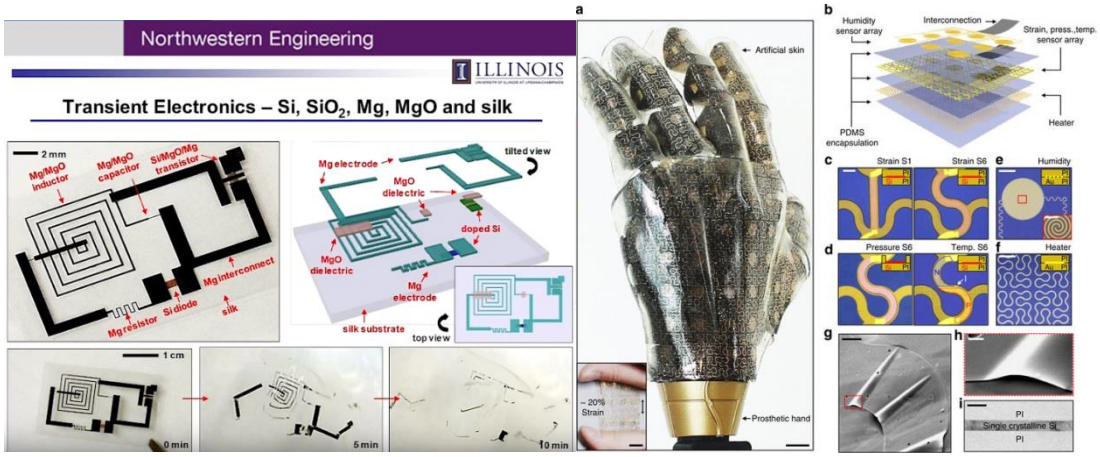


圖 10 薄膜電晶體及傳感連接器應用於人工傳感測簡介

Tuesday Afternoon, May 21, 2019

	Hard Coatings and Vapor Deposition Technologies Room Golden West - Session B7-TuA Plasma Diagnostics and Growth Processes **Moderators: Arutiun P. Ehiasarian**, Sheffield Hallam University, UK, **Yolanda Aranda Gonzalvo**, University of Minnesota, USA	Coatings for Biomedical and Healthcare Applications Room Pacific Salon 3 - Session D2-TuA Bio-corrosion and Bio-tribology **Moderators: Jessica Jennings**, University of Memphis, USA, **Steve Bull**, Newcastle University, UK
1:40pm	**B7-TuA1** On the Growth of TiO_x Coatings by Reactive Magnetron Sputtering from Metallic and Ceramic ($TiO_{1.8}$) Targets: A Joint Modelling and Experimental Story, *R. Tonneau, P. Moskovkin,* University of Namur, Belgium; *W. De Bosscher,* Soleras Advanced Energy, Belgium; *A. Pflug,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany; *S. Lucas,* University of Namur, Belgium	**D2-TuA1** Bio-Tribocorrosive Behavior of the Contact M30NW Stainless Steel against HDPE Reinforced with MoS_2 Particles. New Polymer Implant: Promising Material?, *A. Salem, M. Guezmil, W. Bensalah, S. Mezlini,* Université de Monastir, Tunisia; *J. Géringer,* Mines Saint-Etienne, France
2:00pm	**B7-TuA2** Titanium Atom and Ion Number Density Evolution in Reactive HiPIMS with Oxygen, Nitrogen and Acetylene Gas, *M. Fekete,* Masaryk University, Brno, Czech Republic; *D. Lundin,* Université Paris-Sud/CNRS, France; *K. Bernatova, P. Klein, J. Hnilica, P. Vasina,* Masaryk University, Brno, Czech Republic	**INVITED: D2-TuA2** Evaluation of the Adhesion of Electrosprayed and Solution-Cast Chitosan Coatings on Titanium Surfaces, *V. Suresh, E.J. Chng, J. Bumgardner, R. Gopalakrishnan,* University of Memphis, USA
2:20pm	**B7-TuA3** Phase Formation during Sputtering of Copper in Argon/Oxygen Mixtures, *D. Altangerel, D. Depla,* Ghent University, Belgium	Invited talk continues.
2:40pm	**INVITED: B7-TuA4** Plasma Diagnostics During Growth of Transparent Conductive Oxide Thin Films by Magnetron Sputtering, *E. Stamate,* Technical University of Denmark, Denmark	**D2-TuA4** Study of the Mechanical and Tribological Properties of the TaN with Ti Inclusion Multilayer Films on Si Substrate, *E. García,* Cátedras-CONACyT, Universidad de Guadalajara, México; *J.O. Berumen,* ITESO, Universidad Jesuita de Guadalajara, Tlaquepaque, Jalisco, México; *M. Flores-Martinez,* Universidad de Guadalajara, México; *E. Camps,* Instituto Nacional de Investigaciones Nucleares, México; *S. Muhl,* Instituto de Investigaciones en Materiales-UNAM, México
3:00pm	Invited talk continues.	**D2-TuA5** Enhancement of Tribocorrosion Properties of Ti6Al4V by Formation of a Carbide-Derived Carbon (CDC) Surface Layer, *K.Y. Cheng,* University of Illinois at Chicago, USA; *R. Nagaraj, D. Bijukumar, M.T. Mathew,* University of Illinois College of Medicine, USA; *M. McNallan,* University of Illinois at Chicago, USA

圖 11 Prof. Eugen Stamate Invited talk

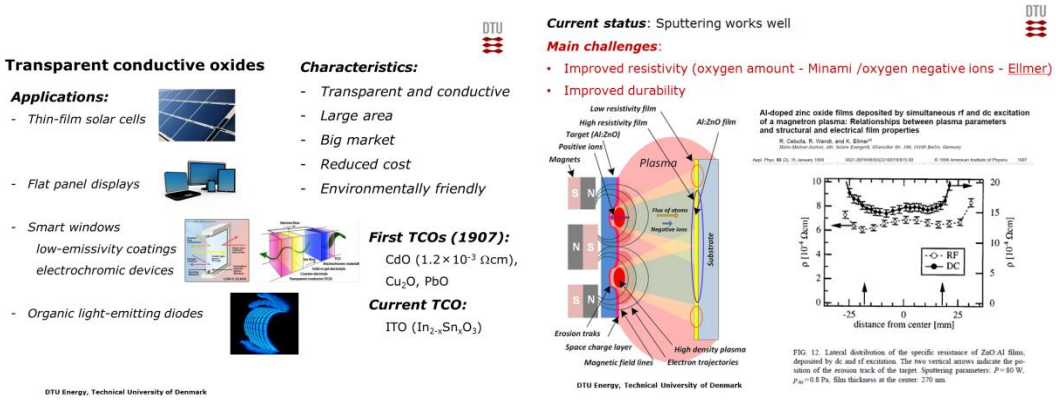


圖 12 介紹透明導電薄膜應用市場及製備透明導電薄膜設備

另外，在 Hard Coatings and Vapor Deposition Technologies 會場上，如圖 11，受邀演講者來至丹麥科技大學 Prof. Eugen Stamate，介紹透明導電薄膜應用市場，如薄膜太陽電池、軟性基板顯示器、低輻射率(Low-E)薄膜、智慧型電致變色膜、有機發光二極體等。皆需要透明導電薄膜製程，如圖 12。Prof. Eugen Stamate 簡報也介紹如何利用電漿診斷技術來監控改善電漿不穩定情形，以及利用不同工作氣壓及氣氛來調控薄膜的結構，為發展反應性鍍膜，尤其金屬氧化物薄膜，之最重要核心關鍵技術。如圖 13 主要說明電漿沉積氧化物反應性鍍膜製程，在長時間鍍膜環境下，電漿會不穩定因而在控制一致性結構實屬不易。因而，設備商開發監控電漿技術及利用不同工作氣壓及氣氛來調控薄膜的結構，如圖 14 與 15。

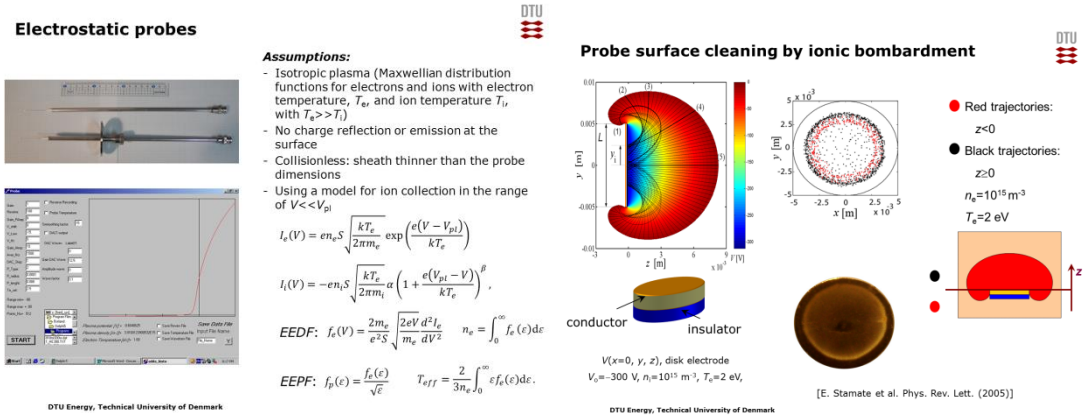


圖 13 電漿探針放入鍍膜系統內診斷電漿能量離化情形及監控電子和離子在 Sheath 區電流分布大小

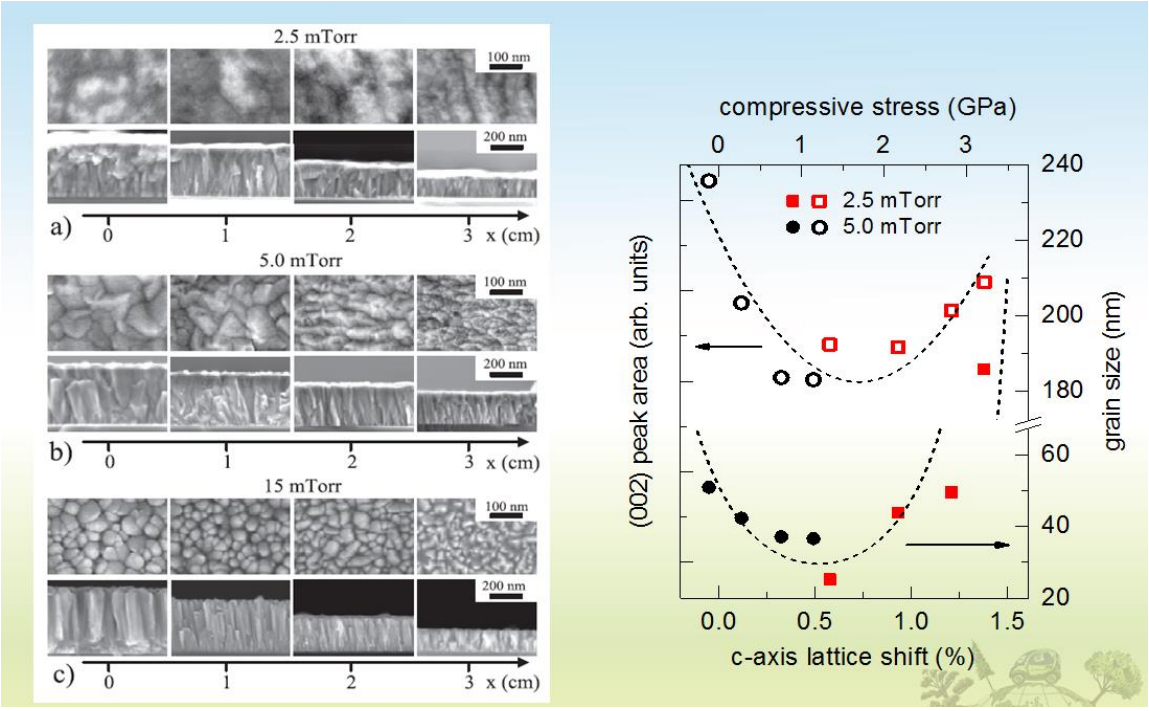


圖 14 利用不同工作氣壓及氣氛來調控薄膜的結構

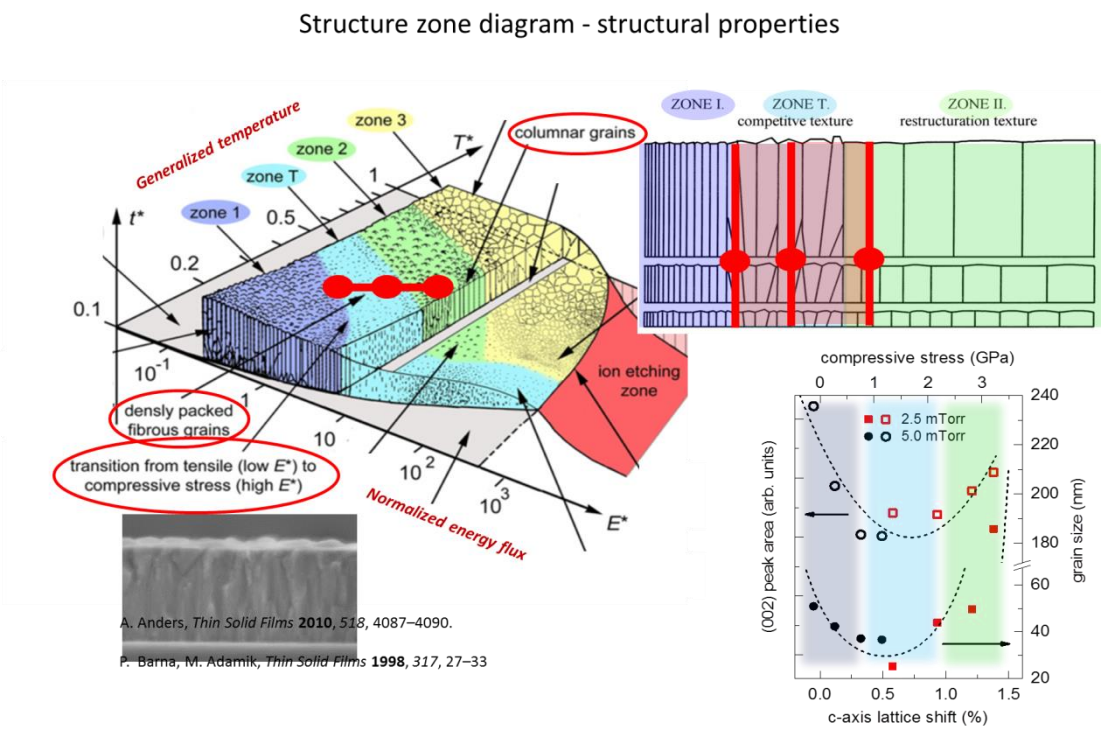
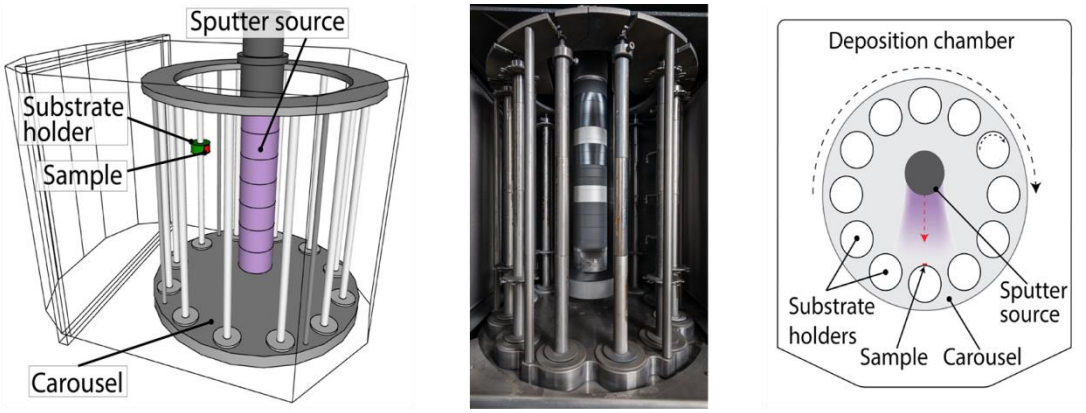


圖 15 利用不同製程溫度及氣壓所分布之薄膜的結構

另外，來自捷克 Prof. M. Kroker 研發磁控脈衝電漿源製備製備 W-B-C 塗層多層(元)結構，如圖 16。作者利用靶鎗上設計不同材料靶材，達到鍍膜所需要的薄膜結構。設計靶鎗之靶材為合成複合材料之最核心技術，尤其想要製作合金材料時，在鍍膜工程上為是否成功之成敗關鍵，如圖 17 與 18。

圖 16 來自捷克 Prof. M. Kroker 簡介 W-B-C 塗層多層結構



Experiments were performed employing industrial sputtering system developed by SHM Sumperk, Czech Republic.

HV chamber (85×55×55 cm) contains planetary table with substrates holders performing multiple axis rotation around central magnetron sputtering cathode.

圖 17 靶鎗上設計不同材料靶材

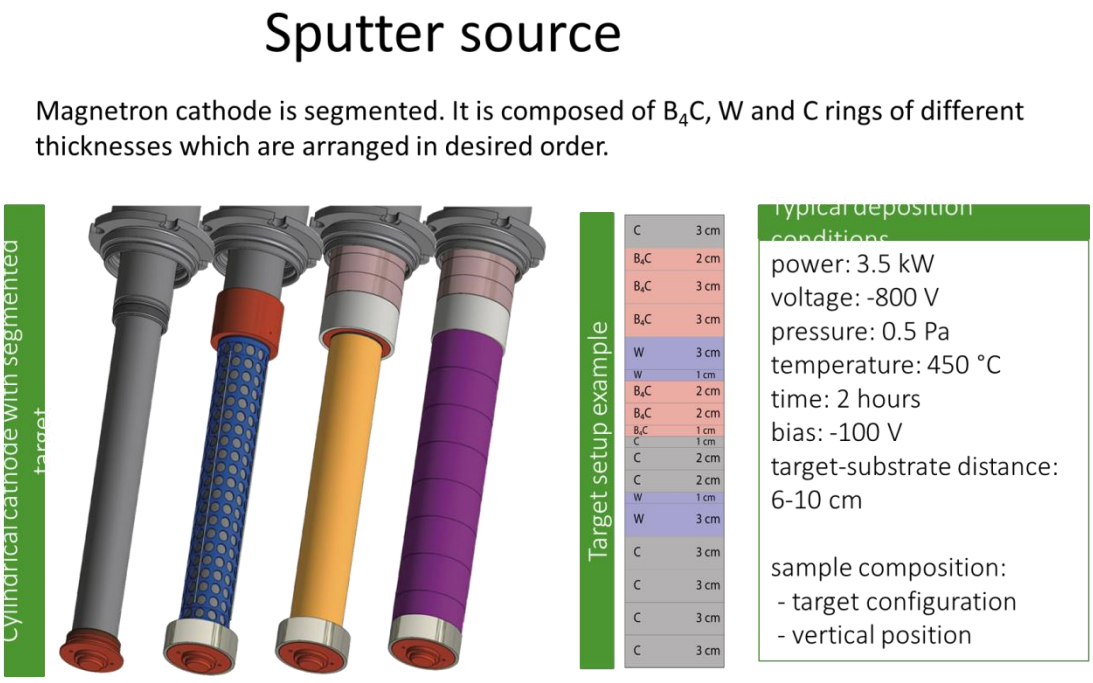


圖 18 介紹由內層到外層把材上之材料結構設計並搭配製程參數製作

另外，也介紹基板在旋轉時與靶材同時旋轉時，如何計算轉動設計概念圖，以達到所需之功能性薄膜。因為靶材在旋轉時，可撓基材亦也跟著再轉動，如圖 19。實驗結果反推合成 W 和 B 的薄膜厚度分析及不同角度沉積薄膜之結構分析，如圖 20 與圖 21。研究也介紹所有實驗皆會先模擬設計是否正確後，再導入實作製作，如圖 22。

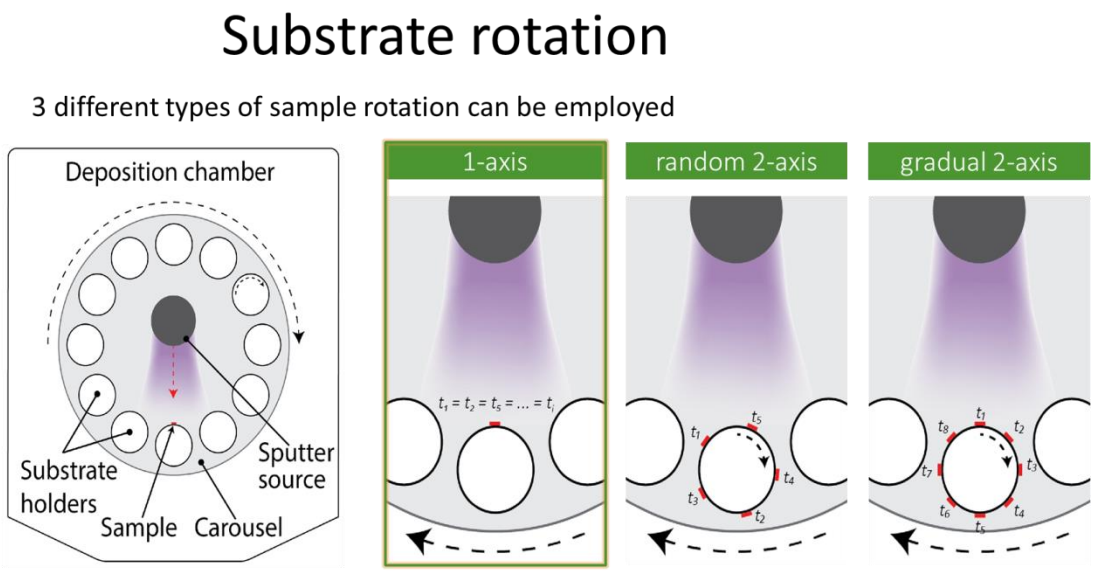


圖 19 簡介 1 維到 2 維空間上公轉及自轉之轉動軸設計

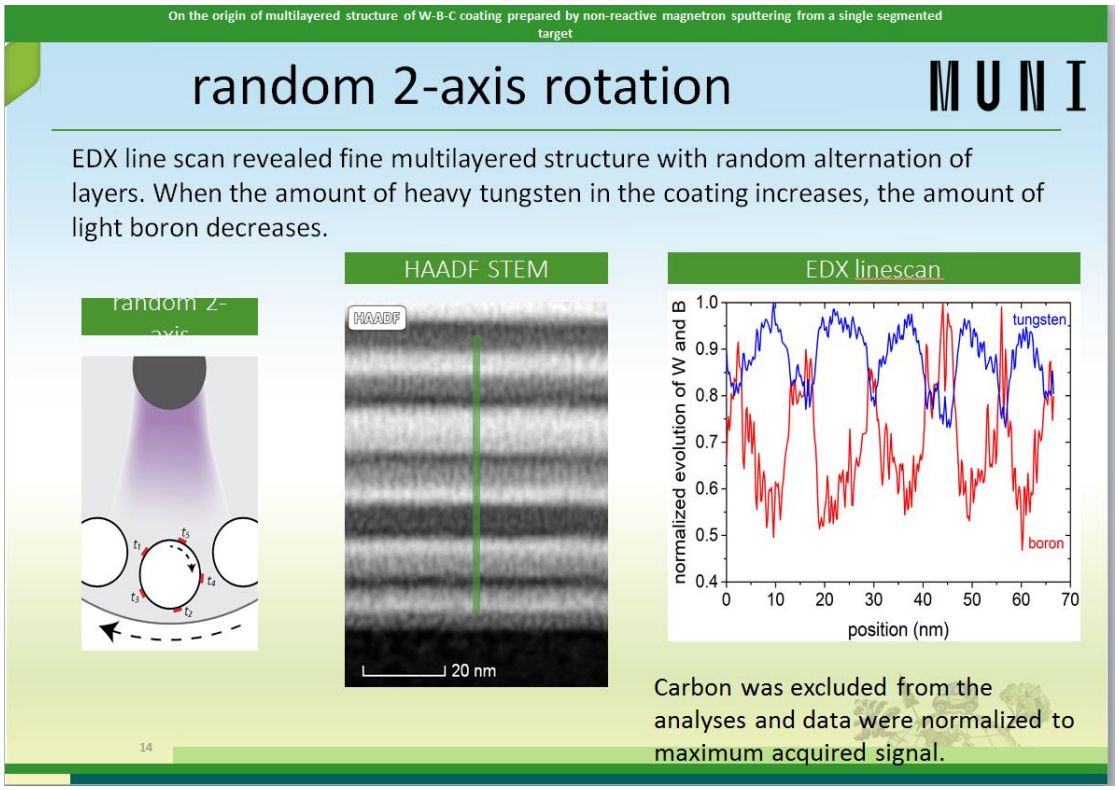


圖 20 分析實驗結果反推合成材料 W 和 B 厚度

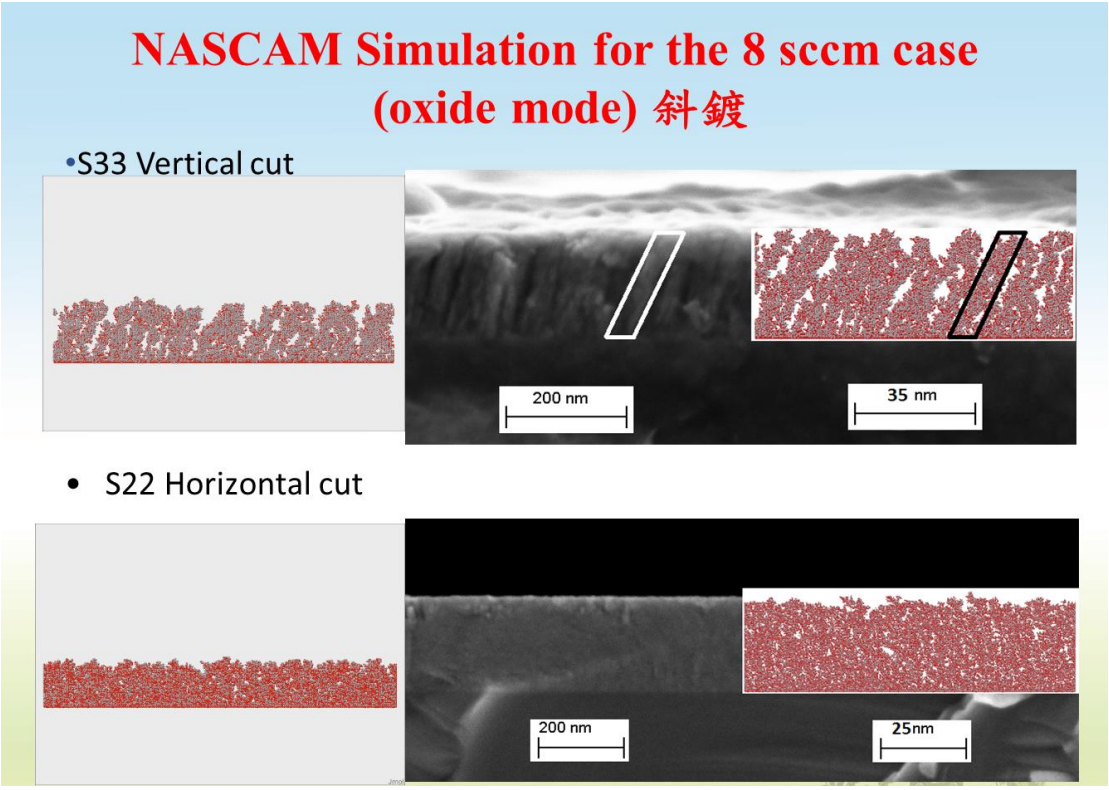


圖 21 不同角度沉積薄膜之結構分析

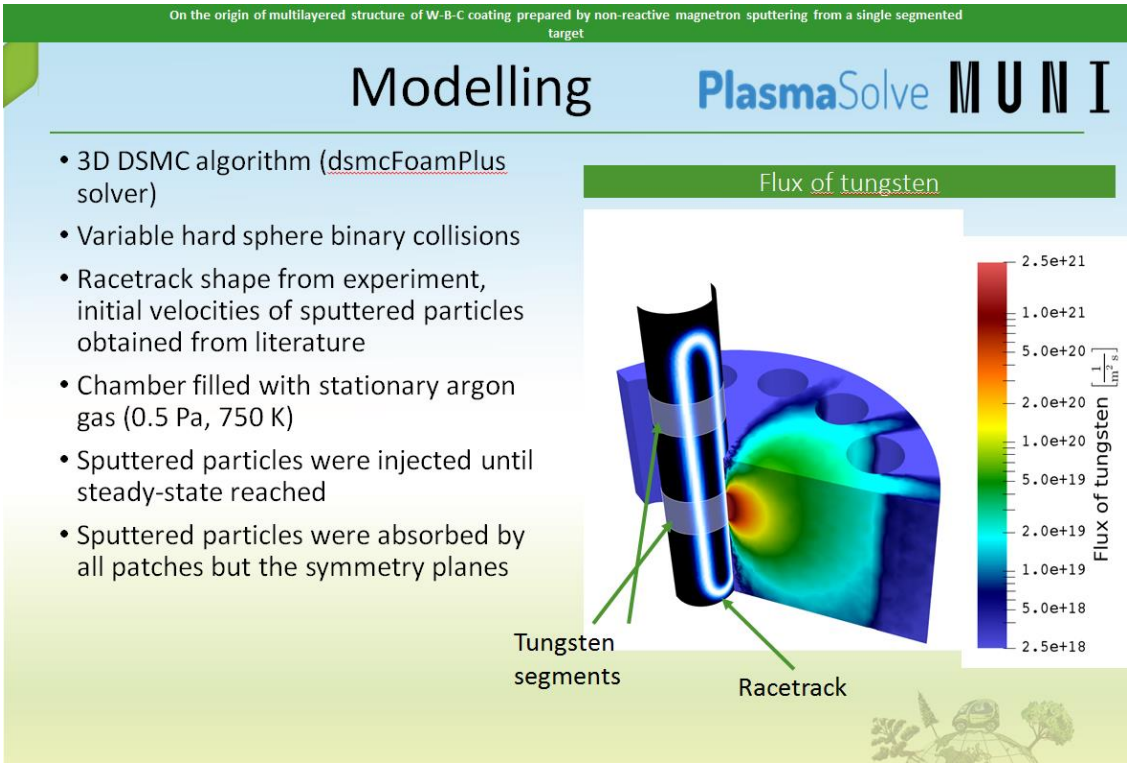


圖 22 藉由模擬設計可轉動靶材之電漿源空間上分布

四、建 議 事 項

(一) 未來建議可開發新型多孔半導體光電薄膜，如二氧化鈦、氧化鎳、氧化鋅、氧化鉬等材料。可藉由高密度電漿製程開發技術，增加比表面積比，形成多孔結構具有特殊功能性。

(二)建議未來電漿設備發展嘗試不同功能性薄膜，諸如記憶合金、開發量子新材料儲能電池或磁性自旋元件等方面進行技術整合與開發應用。

(三)利用多孔性特性概念可導入氣體感測器薄膜開發，如 WO_3 薄膜應用於 H_2 氣體感測器，可以縮短與反應氣體響應時間，預期可以改善磁控濺鍍所面臨到的瓶頸。

(四)建議運用本所高功率磁控脈衝電漿源 (High Power Impulse Magnetron Sputtering, HIPIMS) 真空鍍膜技術結合電漿診斷及監控技術開發多層結構製程。

五、附　錄

附件一、會議安排口頭報告之時程
附件二、會議註冊資料
附件三、投稿全論文

附件一、會議安排口頭報告之時程

Wednesday Morning, May 22, 2019

	Fundamentals and Technology of Multifunctional Materials and Devices **Room Golden West - Session C3+C1-WeM** **Thin Films for Energy-related Applications I/Optical Metrology in Design, Optimization, and Production of Multifunctional Materials** **Moderators: Per Eklund**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Tushar Shimpi**, Colorado State University, USA	**Tribology and Mechanical Behavior of Coatings and Engineered Surfaces** **Room San Diego - Session E3-WeM** **Tribology of Coatings for Automotive and Aerospace Applications** **Moderators: John Curry**, Sandia National Laboratories, USA, **Christian Greiner**, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany, **Oliver Hunold**, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein
8:00am		**INVITED: E3-WeM1** Self-assembly of Ultra-high Strength Nanoporous Metals for Multifunctional Coatings and Free-standing Films, ***J.H. Pikul,*** University of Pennsylvania, USA; *N. Argibay, J. Curry,* Sandia National Laboratories, USA; *Z. Hsain,* University of Pennsylvania, USA
8:20am	**C3+C1-WeM2** Avoiding Blistering of Magnetron Sputtered Thin Film CdTe Photovoltaic Devices, *J.M. Walls, F. Bittau, R.C. Greenhalgh, A. Abbas,* ***P. Hatton,*** *R. Smith,* Loughborough University, UK	Invited talk continues.
8:40am	**C3+C1-WeM3** Electrochromic Device Based on WO_3/NiO Complementary Electrodes Prepared by Using Vacuum Cathodic Arc Plasma, ***P.-W. Chen,*** Institute of Nuclear Energy Research, Taiwan	**E3-WeM3** Elevated Temperature Sliding Wear of PEO-Chameleon Duplex Coating, ***A.A. Voevodin,*** *A. Shirani,* University of North Texas, USA; *A. Yerokhin,* The University of Manchester, UK; *A.L. Korenyi-Both,* Tribologix Inc., USA; *D. Berman,* University of North Texas, USA; *J. Zabinski,* Army Research Laboratory, USA
[illegible]	**C3+C1-WeM4** Influence of Film Thickness on Growth, Structure and Properties of Magnetron Sputtered ITO Films, ***A. Subacius,*** Manchester University, UK; *É. Bousser,* École Polytechnique de Montréal, Canada; *B. Baloukas,* Polytechnique Montreal, Canada; *S. Hinder, M. Baker,* Surrey University, UK; *D. Ngo,* Manchester University, UK; *C.G. Rebholz,* Cyprus University, Cyprus; *A. Matthews,* Manchester University, UK	**E3-WeM4** Formation Mechanisms of Zn, Mo, S and P Containing Reaction Layers on a DLC Coating, *K. Bobzin, T. Brögelmann, C. Kalscheuer,* ***M. Thiex,*** Surface Engineering Institute - RWTH Aachen University, Germany
9:20am	**INVITED: C3+C1-WeM5** Metal/Semiconductor Superlattice Metamaterials: A New Paradigm in Solid-State Energy Conversion, ***B. Saha,*** Jawaharlal Nehru Centre for Advanced Scientific Research, India	**E3-WeM5** ta-C Coatings for Tribological Applications, *J. Becker,* Oerlikon Balzers Coating Germany GmbH, Germany; *N. Beganovic,* ***A. Gies,*** *J. Karner,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *J. Vetter,* Oerlikon Balzers Coating Germany GmbH, Germany
9:40am	Invited talk continues.	**E3-WeM6** Investigation on Effect of MgO-ZrO_2 and Al_2O_3-13%Tio_2 Coated Piston Crown on Performance and Emission Characteristics of a Variable Compression Ratio Engine, ***T. Raja,*** Sri Ramakrishna Institute of Technology, India; *S. Periyasamy,* Government College of Technology, Coimbatore, India
10:00am 10:20am 10:40am	**SESSION BREAK: COMPLIMENTARY REFRESHMENTS IN EXHIBIT HALL**	**SESSION BREAK: COMPLIMENTARY REFRESHMENTS IN EXHIBIT HALL**
11:00am		**E3-WeM10** Titanium Nitrides Coatings for Hard Chromium Replacement, ***M. Cavarroc,*** Safran Tech, France; *B. Giroire, L. Teulé-Gay, D. Michau, A. Poulon-Quintin,* ICMCB, France
11:20am		**E3-WeM11** Tribological Coating Solutions and Lubrication Strategies for Gas Turbine Engines, ***P. Stoyanov,*** Pratt & Whitney, USA
11:40am 12:00pm	**EXHIBIT HALL CLOSES TODAY** **10:00 am – 2:00 pm, Grand Hall** **Enjoy the Light Lunch at 12:20 pm** **(while supplies last)**	

附件二、會議註冊資料

2019/2/12 Confirmation: ICMCTF 2019 - 46th International Conference on Metallurgical Coatings and Thin Films

ICMCTF 2019 Registration Confirmation & Receipt

Confirmation Number: 2275445

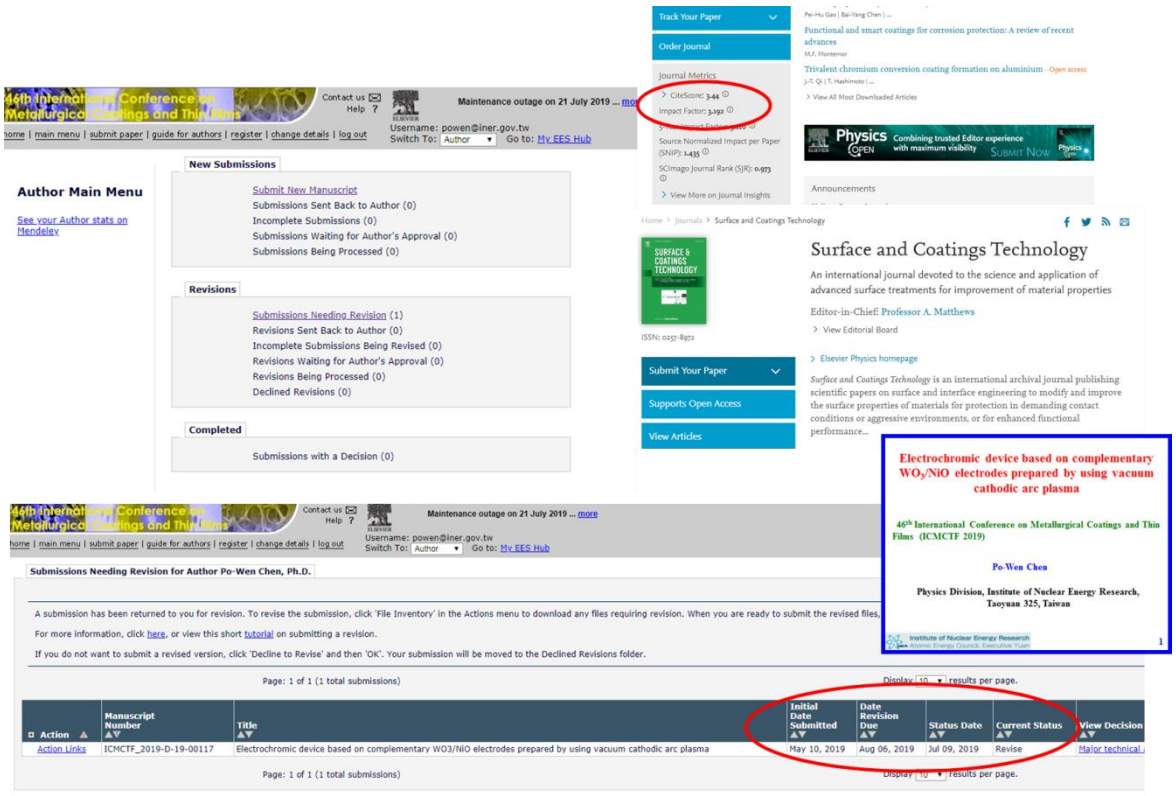
We look forward to seeing you at ICMCTF 2019 - 46th International Conference on Metallurgical Coatings and Thin Films. Please print and present this confirmation at the conference registration counter to pick up your conference materials onsite. Note that all registrants will be required to show a valid ID at the registration counter. Student registrants will be required to show a valid student ID. San Diego area registrants will need to show a valid San Diego area ID (i.e., CA Driver's License with San Diego area zip code or other proof of residence).

Registrant Details

Full Name	Company/Affiliation	Registrant Type	Price
PO-WEN CHEN	Institute of Nuclear Energy Research, Atomic Energy Council	Regular Early - Hotel	$750.00

Registration Selections

Selection	Quantity	Unit Price	Total
Regular Early - Hotel	1	$750.00	$750.00
		Total	**$750.00**



附件三、投稿全論文

Electrochromic device based on complementary WO_3/NiO electrodes prepared by using vacuum cathodic arc plasma

Po-Wen Chen [1,*], Sheng-Chuan Hsu [1], Chen-Te Chang[1], Tien-Fu Ko[1], Jin-Yu Wu[1], Wen-Fa Tsai[1], and Hwen-Fen Hong[1]

[1] **Division of Physics, Institute of Nuclear Energy Research, Taoyuan County 32546, Taiwan**

* **Correspondence: powen@iner.gov.tw;**

Abstract: In this study, we prepared a complementary electrochromic device (ECD) with ITO/WO_3/LiClO4-PC/NiO/ITO structure. This work focues on the influence of thickness of WO_3 layers on the ECD electrochemical and optical properties. For the fabrication of ECD, WO_3 and NiO electrode films were used as the cathodic and anodic coloring materials, which are fabricated by vacuum cathodic arc plasma (CAP). We achieve a high performance electrochromic elecrode, producing porous deposited by the CAP technique is promising smart window for potential electrochromic application. Our results of WO_3/ITO films are observed the highest oxidation/reduction ion diffusion coefficient (7.36×10^{-10} and 4.92×10^{-10} cm^2/s respectively) with WO_3 (200 nm)/ITO films, meaning that enhanced electrochromic properties compared to the other samples. The performance of the 3×4 cm^2 ECD demonstrated optical contrast of 46% and switching times 4.6 sec and 3.1 sec for coloring and bleaching state at the wavelength of 633 nm. During the durability test, the transmittance cahnge (ΔT) of ECD remained 43% after 2500 cycles, which was about 90% of original state.

Keywords: Tungsten oxide (WO_3) film; nickel oxide (NiO) film; Electrochromic device (ECD); Cathodic arc plasma (CAP)

1. Introduction

Electrochromism refers to an interesting phenomenon that materials change their optical characteristics (transmittance, reflectance and absorption) reversibly through applying a dc voltage [1]. For the past decades, various electrochromic materials have been developed, including metal oxides [2-4], small organic molecules [5], and conductive polymer thin films [6-8]. Electrochromic device (ECD) can be categorized into three types: solution type, hybrid type, and thin-film battery-like type. ECD can find applications in smart windows, energy efficient buildings, optical information displays, variable-reflectance mirrors, switchable mirrors, and electronic papers [9-11]. A complementary ECD is composed of one anodic and cathodic coloring/bleaching material [12]. A basic multi-layer ECD consists of five layers with an ionic conduction layer (electrolyte) in contact with an Electrochromic (EC) layer and an ion storage (complementary) layer, all sandwiched between two transparent conducting layers, the physical structure is shown in the 3D schematic diagram illustrated in Fig. 1. The complementary ECD offers great advantage, such as fast coloration, high coloration efficiency and low energy consumption [12]. The complementary ECD offers great advantage, such as fast coloration, high coloration efficiency and low energy consumption [12]. Tungsten oxide (WO_3) is known as one of the most popular cathodic coloration material and nickel oxide (NiO) as typical anodic coloration material, which have been intensively investigated [13-14]. WO_3 and NiO can be fully transparent to visible light, and they are quite complementary due to the simultaneous modulation.

The transition metal oxides, WO_3 film is the key point studied in this article. WO_3 film is widely application potential and can switch between colorless and blue color reversible by alternately applying a small positive and negative voltage [15, 16]. The electrochromic chemical reaction of WO_3 film is based on reversible oxidation/reduction reactions induced by electrochemical double injection/extraction of positive ions (lithium or proton) and electrons into/outside the host of WO_3 lattice in transition of W^{5+} and W^{6+} [16]. To data, a variety nanostructure of WO_3 film is included that nano-rods [17], nanosheets [18], and nanotree [19] have fabricated in that literature. Typically, nanostructures are desired its higher specific surface area and porosity, are the most suitable for electrochromic applications and could be increasing the contact area between the electrode and electrolyte since reduced the diffusion path of ions [17-19].

The electrochromic WO_3 film has been fabricated by various methods, such as sputtering [20-21], chemical vapor deposition (CVD) [22-23], spray pyrolysis [24-25],

thermal evaporation [26-28], electron-beam deposition [29], and sol-gel [30-32] methods. Recently, Lee [17] *et al.* reported that uniform WO_3 nanorods were successfully synthesized in which it is shown fast coloration/bleaching times (28.8/4.5 sec) at 633 nm. Zhang [19] *et al.* synthesized one-dimensional structure WO_3 electrodes via thermal annealing treated shown as well as good CE (43.6 cm^2/C), and fast coloration/bleaching times (7.6/4.2 sec) at 633 nm.

In this study, we have developed a method of CAP deposition technique owns a high deposition rate and CAP source target poisoning less than the sputtering case. Furthermore, this method with low-cost advantage has great commercial potential application. We synthesized nanostructure of WO_3/NiO films via CAP technique. This work focuses on fabricating cathodic WO_3 film through four different thicknesses. In this study focuses on the influence of thickness of WO_3 layers on the ECD electrochemical and optical properties. We prepared a complementary electrochromic device (ECD) with ITO/WO3/$LiClO_4$-PC/NiO/ITO structure.

2. Experimental

2.1 Preparation electrochromic and transparent films

Indium tin oxide (ITO) glass was used as substrate, and the sheet resistance is about 6.1 Ω/□. ITO glass was cleaned by ultrasound in deionized water and ethyl alcohol for 2 min in turns. We used metallic tungsten (W) target (99.95%) and Nickel (Ni) target (99.95%). The WO_3 film was deposited on ITO/glass substrate by using cathodic arc plasma (CAP) deposition with a purity tungsten (W)-metal target (76 mm in diameter and 12 mm in thickness) at room temperature. In this study, we used an oxygen mass flow of 375 sccm and argon mass flow of 75 sccm for the reactive gases. The NiO film was deposited on ITO/glass substrate by using cathodic arc plasma (CAP) deposition with a purity nickel (Ni)-metal target (76 mm in diameter and 12 mm in thickness) at 50^0C. The base chamber pressure was set to be less than 2×10^{-5} Torr using turbo pump. The WO_3/NiO and ITO series were fabricated on ITO/glass as electrochromic layers, which are listed in Table 1 and 2.

Table 1

Detail of WO_3 processing parameters of with various thicknesses

WO_3 Processing	Working Pres. (Torr)	Base Pres. (Torr)	Ar/O_2 (sccm)	DC Power (W)	Thickness (nm)	Time (min)	Deposition Temp. (^{o}C)	Deposition Rate. (nm/min)
Sample-1	$8.3x10^{-3}$	$1.2x10^{-5}$	0.2	1250	175	11	RT	15.9
Sample-2	$8.3x10^{-3}$	$1.2x10^{-5}$	0.2	1250	200	13	RT	15.4
Sample-3	$8.3x10^{-3}$	$1.2x10^{-5}$	0.2	1250	225	15	RT	15.0

Sample-4	$8.3x10^{-3}$	$1.2x10^{-5}$	0.2	1250	250	17	RT	14.7

RT*: Room temperature.

Table 2

More details of ECD on the deposition parameters are presented in Table.

Target	**Working Pres. (Torr)**	**Base Pres. (Torr)**	**Ar/O_2 (sccm)**	**DC Power (W)**	**Thickness (nm)**	**Time (min)**	**Deposition Temp. (^oC)**	**Deposition Rate. (nm/min)**
ITO	$3x10^{-3}$	$8.5x10^{-6}$	100	500	300	60	200	5
Metal Ni	$8.3x10^{-3}$	$1.2x10^{-5}$	1/3	650	50	2.5	50	20

2.2 Electrolyte layer

In the electrolyte system, we used liquid electrolyte composed of lithium perchlorate (LiClO4, M_w = 106.39, Sigma-Aldrich, Darmstadt, Germany) and propylene carbonate (PC, $C_4H_6O_3$, Sigma-Aldrich), the resulting weight ratio was 0.1325 ($LiClO_4$/ PC = 26.5 g/200 mL).

2.3 Measurements

The cycle voltammetry (CV) and chronoamperometry (CA) measurements were performed in order to understand the electrochemical properties of the electrochromic films/ECDs using a potential/galvanostat (model PGSTAT30, Autolab). The optical transmittance modulation for ECD was measured using a UV-Vis spectrometer (USB 4000, Ocean Optics, Inc. 830 Douglas Ave. Dunedin, USA).

2.4 Assembly and characterization of the ECDs

We chose 0.5 M $LiClO_4$/PC solution as the electrolyte for ECDs. This work focuses on fabricating WO_3/NiO as working/counter electrodes deposited by CAP deposition. In this report, we demonstrate a high-performance active area of 3×4 cm^2 composed of glass/ITO/WO_3/liquid electrolyte/NiO/ITO/glass, which key factor WO_3 film with various thicknesses (175 nm, 200 nm, 225 nm, and 250 nm) exhibits improved electrochrmic properties. The schematic diagram of the ECD is shown in Fig. 1.

(a) (b)

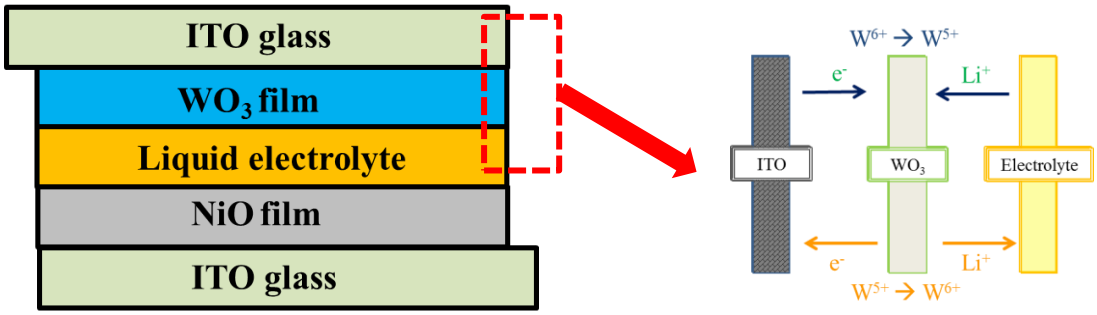


Fig. 1. (a) Schematic diagram of the electrochromic device (b) Key factor WO_3 films the reduction of W-ions W^{6+} to W^{5+} led to coloring state, and the oxidation of W^{5+} to W^{6+} caused a bleaching phenomenon.

3. Results and Discussion

3.1 Characterization of cyclic voltammetry with various thicknesses WO_3/ITO films

This work focues on the influence of thickness of WO_3 layers (175 nm, 200 nm, 225 nm and 250 nm) on the ECD electrochemical and optical properties. To understand the electrochemical properties of WO_3/ITO/glass, CV measurements were performed by constructing three electrode cells consisting of a working electrode (WO_3 electrodes film deposited on ITO/glass) and a counter-electrode (Pt mesh) in 0.5 M $LiClO_4$/PC solution. The CV curve of the current density and voltage traces were recorded within a linear potential sweep between −1.5 V (coloration) and 0.3 V (bleaching) at a fixed scan rate 200 mV/s. The coloration/bleaching electrochromic processes involved the injection/extraction of Li^+ ions into/out of the WO_3 electrode film following electrochemical reaction:

$$WO_3\ (\text{bleaching}) + x\ (Li^+ + e^-) \rightarrow Li_xWO_3\ (\text{coloration}). \quad (1)$$

During the cathodic scan, the reduction of W-ions W^{6+} to W^{5+} led to coloring state, and the reverse anodic scan (forward scan) the oxidation of W^{5+} to W^{6+} caused a bleaching phenomenon. When applying the negative voltage on the WO_3 electrode film, the electrons and Li^+ ions were inserted into the WO_3 crystal structure, and W^{6+} reduced to a lower valence state W^{5+}, as shown by the tungsten bronze structure Li_xWO_3 (coloration state) shown in Fig. 1 (b) [16]. The 25th-cycle CV curves of key factor WO_3 films with various thicknesses (175 nm, 200 nm, 225 nm, and 250 nm) are shown in Fig. 2. The diffusion coefficients of Li^+ ions in WO_3/ITO films could be evaluated by measuring the CV curves, and diffusion coefficients were a representative parameter to evaluate the structural properties of the films. The relationship between the peak current and the scan rate could be determined with the Randles–Servick equation for relating ion diffusion coefficients [17] as follows:

$$J_p=2.69\times10^5 n^{3/2} C_0 D^{1/2} v^{1/2} \quad (2)$$

Sample	Thickness (nm)	Anodic Peak current(j_{pa})	Cathodic Spike Current(j_{pc})	Diffusion Coefficient(cm^2/s) D for i_{pa}	D for i_{pc}
1	175	1.19E-03	9.28E-04	3.9242E-10	2.38E-10
2	200	1.63E-03	1.33E-03	7.35952E-10	4.92E-10
3	225	1.41E-03	1.14E-03	5.45959E-10	3.62E-10
4	250	1.10E-03	8.90E-04	3.36344E-10	2.19E-10

where C_0 is the concentration of the active ions in the electrolyte solution in $mol \cdot cm^{-3}$; v is the potential scan rate Vs^{-1}; D is the diffusion coefficient in cm^2s^{-1}, J_p is the peak current density in unit of area (working area 3×4 cm^2), which includes J_{pc} and J_{pa} with oxidation and reduction of peak current density; and n is the number of electrons *participated* in the chemical reaction. The J_{pc}, J_{pa}, and the diffusion coefficient (D) are shown in Table 3.

Table 3 The diffusion coefficients of WO_3/ITO films with various thicknesses

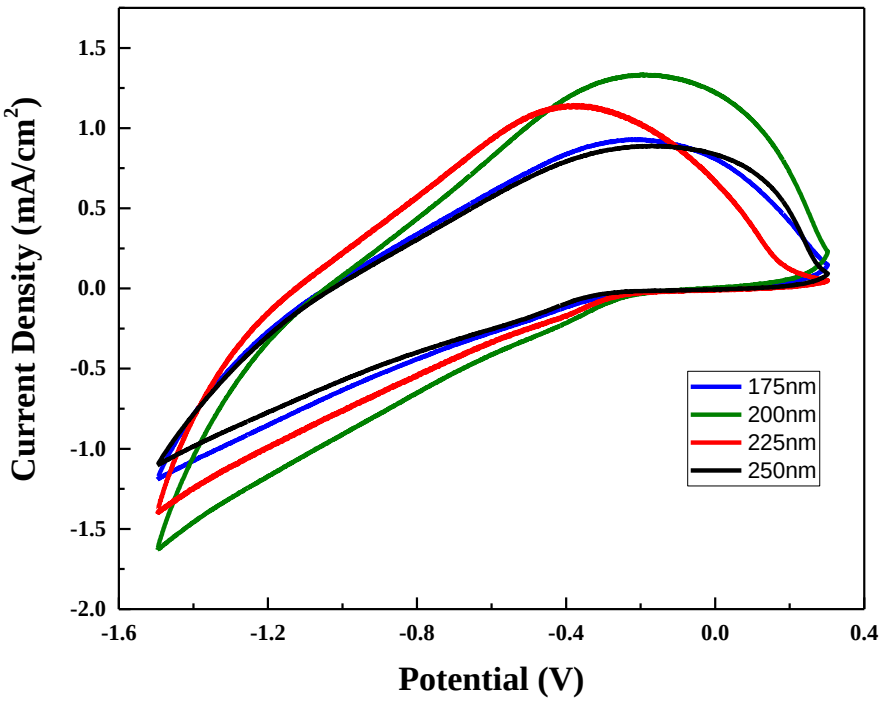


Fig.2 The 25th-cycle CV curves of key factor WO_3 films with various thicknesses.

From Table 3, the resulting higher diffusion coefficients indicate a larger contact area and porosity with fast ion insertion/extraction. We observed the highest oxidation/reduction ion diffusion coefficients (7.36×10^{-10} and 4.92×10^{-10} cm^2/s respectively) with 200 nm WO_3 film, the cathodic and anodic peak currents of the porous film indicated enhanced higher electrochemical activity compared to the other samples. In order to quantify electrochromic performance of WO_3 film, the transmittance spectra in colored and bleached states were measured under an applied potential of -1.5 and 0.3 V (*vs.* Ag/AgCl) at a scan rate 200 mV s^{-1}. The color of WO_3 film changes from dark blue (colored state) to transparent (bleached state) reversibly.

Fig. 3, the optical transmittance spectra of WO_3/ITO films between bleaching and coloration states with different thicknesses. Furthermore, transmittance optical modulation ($\Delta T = T_{bleaching} - T_{coloration}$) for all samples are shown in Table 4. The optical transmittance changes of all sample increased from 51% to 58.1% at a fixed wavelength of 633 nm as a function of thicknesses. The transmittance optical modulation, ΔT = 58%, with 200 nm WO_3 film was higher than the other samples. The transmittance modulation increased due to a larger enveloped area in the CV curve. Actually, the area of the CV curve is deeply related to the charge stored (capacity) at porous WO_3 film [18] indicates that more charges are taking part in redox reactions.

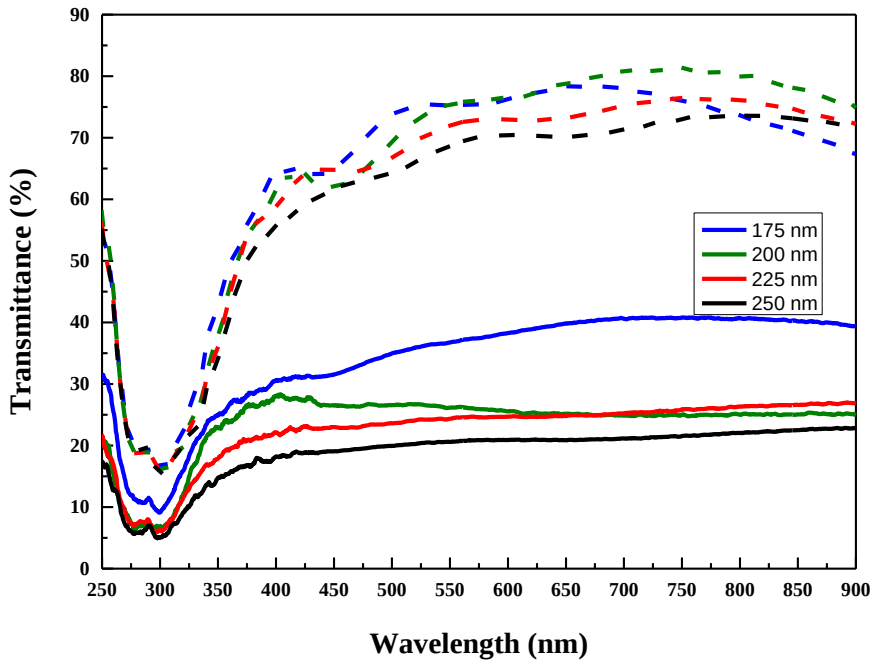


Fig. 3. Transmittance of WO_3 film in bleaching (dotted line) and coloration (solid line) state at different thicknesses.

Table 4 Electrochromic properties of WO_3/ITO film with various thicknesses

Sample (nm)	$T_{bleached}$ (%)	$T_{colored}$ (%)	ΔT (%)	Inserted charge (mC/ cm^2)	Coloration efficiency (cm^2/C)
175	77	26	51	29.2	79.8
200	77	19	58	29.0	90.0
225	73	14.9	58.1	38.2	77.5
250	70	12.4	57.6	43.5	72.3

Coloration efficiency (CE), the important criterion for ECD, is defined the change of optical density (ΔOD) by per unit of inserted charge or extracted charge ΔQ (ΔQ=Q/A, where A is the active area of the device). It can be calculated according the following formulas:

$$CE = \Delta OD/(\Delta Q)$$

$$\Delta OD = \ln(T_{bleached}/T_{colored}) \quad (3)$$

where T_b and T_c refers to the transmittance of the WO_3 film in the bleached and colored state, respectively.

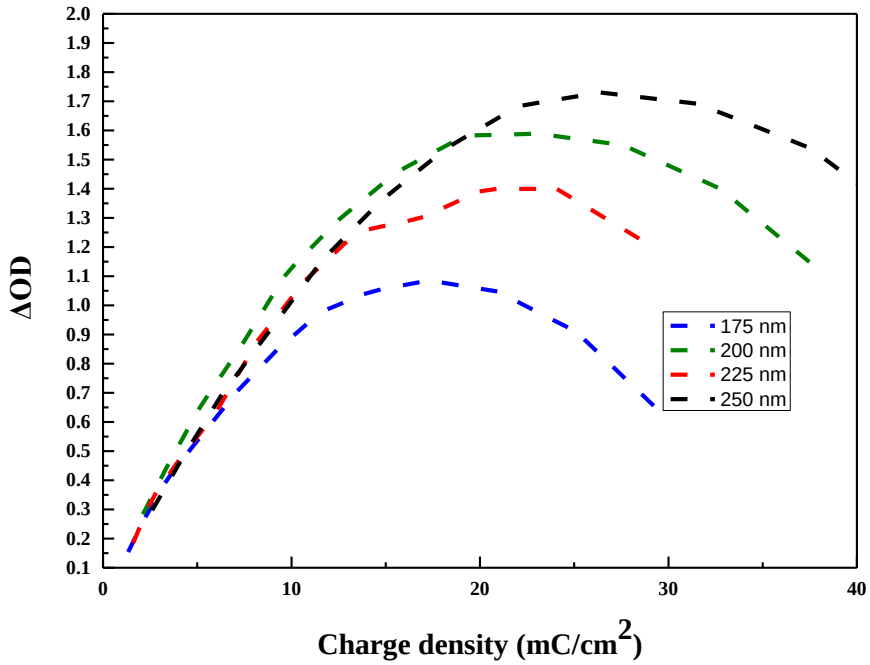
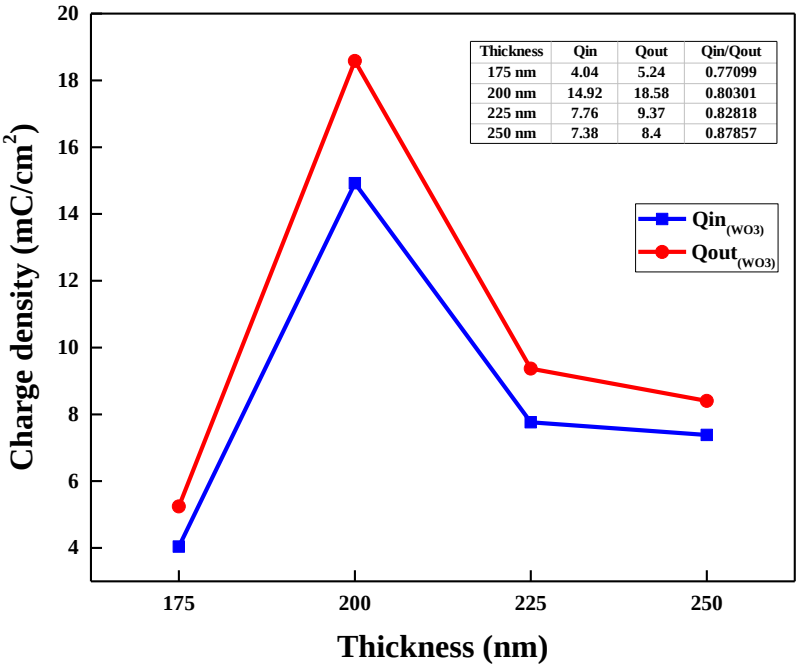


Fig. 4. Optical density change as a function of inserted charge for WO_3/ITO film with various thicknesses.

Fig. 4 shows the plots of ΔOD at a wavelength of 633 nm versus the inserted charge with various thicknesses. From the slope of these curves, the CE value is evaluated. The WO_3 film with 200 nm exhibits enhanced CE of 90 cm^2/C was higher

than the other samples. A high value of CE indicates that the electrochromic materials exhibit a large optical modulation with a small intercalation charge density. The enhanced transmittance modulation and excellent CE of WO_3/ITO film is impressive values as listed in Table 4.

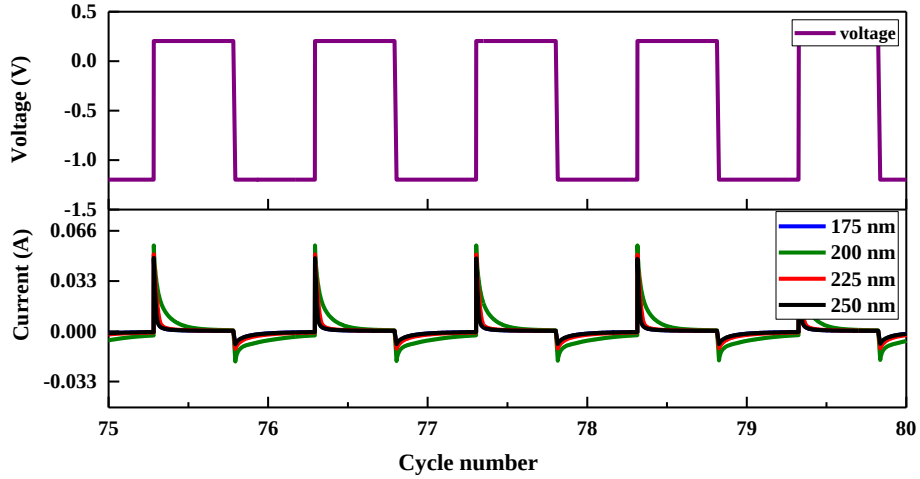


Thickness	Qin	Qout	Qin/Qout
175 nm	4.04	5.24	0.77099
200 nm	14.92	18.58	0.80301
225 nm	7.76	9.37	0.82818
250 nm	7.38	8.4	0.87857

3.2 Characterization of cyclic voltammetry with various thicknesses WO_3/ITO films

The switching kinetic of coloration and bleaching of WO_3/NiO films were investigated by CA measurements.

The complementary ECD has two electrochromic electrode films, similar to Li+ batteries, the change capacity ratio of two electrodes should be qualified determines.



3.3 Characterization of WO_3/NiO ECD

In Fig. # shows the *situ* transmittance of Wo3/NiO ECD at 633 nm is analyzed during the continuous potential cycle from -1.2 V (colored potential, Vc) to 0.8 V (bleaching potential, Vb). ECD shows a maximum optical contrast at 633 nm wavelength, where the change in transmittance (ΔT) reached 43 %. The long-term stabilities of ECD is illustrated in Fig. # b. The interval of each step was controlled at 15 s. No significant degradation of the ECD was notice after 1000 cycles (about 10 hours) as shown in Fig. #. In Fig. #, beginning 1000 cycles of transmittance of bleached/colored states decrease continuously damage in ECD. After 4000 cycles, Wo3/NiO ECD shows poor stability, which reminded only 70/75% and 29/31% of their original bleached and colored respectively.

Fig. #

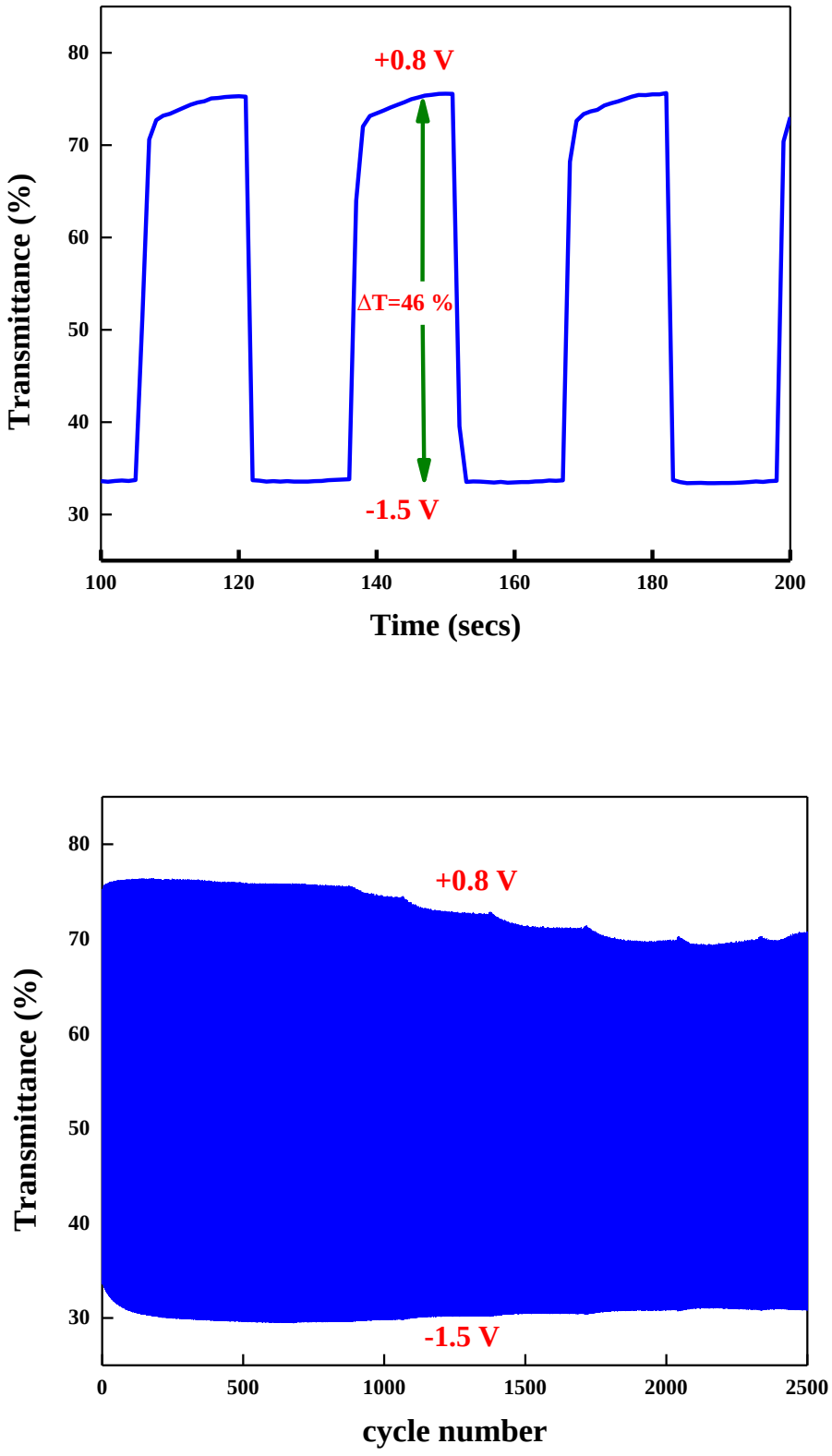

+0.8 V
ΔT=46 %
-1.5 V
Transmittance (%)
Time (secs)
80
70
60
50
40
30
100
120
140
160
180
200
+0.8 V
-1.5 V
Transmittance (%)
cycle number
0
500
1000
1500
2000
2500

Fig. 5. (a)

4. Conclusions

Acknowledgments

PWC would also like to acknowledge support from Division of Physics, Institute of Nclear Energy Research, Taiwan.

5. References

[1] D. R. Rosseinsky, R. J. Mortimer, Electrochromic systems and the prospects for devices, Adv. Mater.13 (2001) 783–793.

[2] C. G. Granqvist, Electrochromic tungsten oxide films: review of progress 1993 -1998, Sol. Energy Mater. Sol. Cells 60 (2000) 201–262.

[3] M. Vidotti, S. I. Córdoba de Torresi, Electrostatic layer-by-layer and electrophoretic depositions as methods for electrochromic nanoparticle immobilization, Electrochim. Acta 54 (2009) 2800–2804.

[4] I. Bouessay, A. Rougier, P. Poizot, J. Moscovici, A. Michalowicz, J. M. Tarascon, Electrochromic degradation in nickel oxide thin film: a self-discharge and dissolution phenomenon, Electrochim. Acta50 (2005) 3737–3745.

[5] Y. Watanabe, K. Imaizumi, K. Nakamura, N. Kobayashi, Effect of counter electrode reaction on coloration properties of phthalate-based electrochromic cell, Sol. Energy Mater. Sol. Cells 99 (2012) 88–94.

[6] T. Kobayashi, H. Yoneyama, H. Tamura, Polyaniline film-coated electrodes as electrochromic display devices, J. Electroanal. Chem.161(1984) 419–423.

[7] A. J. C. Silva, S. M. F. Ferreira, D. D. P. Santos, M. Navarro, J. Tonholo, A. S. Ribeiro, A multielectrochromic copolymer based on pyrrole and thiophene derivatives, Sol. Energy Mater. Sol. Cells 103 (2012) 108–113.

[8] T. Augusto, E. T. Neto, A. A. T. Neto, R. Vichessi, M. Vidotti, S. I. Córdoba de Torresi, Electrophoretic deposition of Au@PEDOT nanoparticles towards the construction of high-performance electrochromic electrodes, Sol. Energy Mater. Sol. Cells 118 (2013) 72–80.

[9] C. M. Lampert, Large-area smart glass and integrated photovoltaics, Sol. Energy Mater. Sol. Cells 76 (2003) 489–499.

[10] E. S. Lee, D. L. DiBartolomeo, Application issues for large-area electrochromic windows in commercial buildings, Sol. Energy Mater. Sol. Cells 71 (2002) 465–491.

[11] B. P. Jelle, G. Hagen, Transmission spectra of an electrochromic window based on polyaniline, Prussian blue and tungsten-oxide, J. Electrochem. Soc. 140 (1993) 3560–3564.

[12] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, the Netherlands, 1995.

[13] X. H. Xia, J. P. Tu, J. Zhang, X. L. Wang, W. K. Zhang, H. Huang, Electrochromic properties of porous NiO thin films prepared by a chemical bath deposition, Sol. Energy Mater. Sol. Cells 92 (2008) 628–633.
[14] A. Subrahmanyam, C. S. Kumar, K. M. Karuppasamy, A note on fast protonic solid state electrochromic device: $NiO_x/Ta_2O_5/WO_3$-x, Sol. Energy Mater. Sol. Cells 91 (2007) 62–66.
[15] Z. Xie, L. Gao *et al.*, Fast fabrication of a WO3˙H2O thin film with improved electrochromic properties, J. Mater. Chem., 22 (2012), 19904-19910.
[16] G. A. Niklasson and C. G. Granqvist, Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these, J. Mater. Chem., 17 (2007), 127-156.
[17] E. Khoo, P. S. Lee, J. Ma , Electrophoretic deposition (EPD) of WO_3 nanorods for electrochromic application, J. Eur Ceram Soc, 30 (2010), 1139.1144.
[18] J. Zhang, X. L. Wang, X. H. Xia, *et al.*, Electrochromic behavior of WO_3 nanotree films prepared by hydrothermal oxidation, Sol. Energy Mater. Sol. Cells 95 (2011), 2107-2112.
[19] B. Liu, J. Wang, J. Wu, *et al.*, Controlled fabrication of hierarchical WO_3 hydrates with excellent adsorption performance, J. Mater. Chem. A, 2 (2014), 1947-1954.
[20] D. Deniz, D. J. Frankel and R. J. Lab, Thin Solid Films, 518 (2010), 4095.
[21] M. H. Yaacob, M. Breedon, K. Kalantar-Zadeh *et al.*, Sens. Actuators, B, 137 (2009), 115.
[22] Y. S. Lin, S. S. Wu and T. H. Tsai , Sol. Energy Mater. Sol. Cells, 94 (2010), 2283.
[23] C. M. White, D. T. Gillaspie, E. Whitney, S. H. Lee and A. C. Dillon, Thin Solid Films, 517 (2009), 3596.
[24] S. R. Bathe and P. S. Patil, Sol. Energy Mater. Sol. Cells, 91 (2007), 1097.
[25] P. M. Kadam, N. L. Tarwal, P. S. Shinde, R. S. Patil, H. P. Deshmukh and P. S. Patil, Appl. Phys. A: Mater. Sci. Process., 97 (2009), 323.
[26] J. Thangala, S. Vaddiraju *et, al.*, Small, 3 (2007), 890.
[27] K. J. Patel, C. J. Panchal et *al.*, Mater. Chem. Phys., 124 (2010), 884.
[28] H. D. Zheng, J. Z. Ou *et al.*, Adv. Funct. Mater., 21(2011), 2175.
[29] J. T. Li, M. Toth, V. Tileli *et al.*, Appl. Phys.Lett., 93 (2008), 023130.
[30] W. Wang, Y. X. Pang and S. N. B.Hodgson, J. Mater. Chem., 20 (2010), 859.
[31] H. Fan, A. Wright, J. Gabaldon *et al.*, Adv. Funct. Mater., 16 (2006), 891.
[32] Z. Xie, Y. G. Zhu *et al.*, CrystEngComm, 13 (2011), 6393.