出國報告（出國類別：國際會議）

第 223 屆電化學國際研討會

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摘要

第 223 屆電化學國際研討會(223 ECS meeting) 於 5 月 12 日至 17 日在加拿大多倫多 舉行, 於此爲期六天之會議技術內容涵蓋電化學,固態科學與技術, 其包含七大領域。在七大領域中, 筆者主要參加借電與半導體領域之材料, 元件與製程, 並發表三篇論文與一篇海報張貼, 其中有一篇論文爲邀請演講，會中與與會者互相討論, 交換研究心得, 獲益良多。

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一、目的

此一研討會涵蓋全球領先之電化學、奈米材料、新能源、光電子、生醫光電與綠色光電子領域等，內容包羅萬象，主題新穎。展覽主要爲電化學設備與材料檢測系統，不同領域之相關研究學者，可互相吸收對方之訊息，異業結合更能開創出新的領域與應用。本次參加研討會主要目的爲發表本實驗室今年度最新之研究成果；包括口頭報告論文兩篇:以乾蝕刻搭配濕式蝕刻所研製出具結晶面之圖型化藍寶石基板，其磊晶發光二極體特性之提升，與以犧牲層分離太陽能電池研製出最高效率與最低價格之薄膜型太陽能電池，海報張貼論文一篇:以表面粗化用以提升薄膜型紅光發光二極體之發光效率。藉此論文發表與聆聽相關領域之學者報告其研究成果，藉此一研討會吸收最新研究新知，並與相關研究學者交換研究心得。此外，因筆者也是此一研討會之主持人之一，藉此研討會與國外此一研討會之負責人分享 call for papers 之過程，討論下一年度應該注意之事項。整體而言，無論在論文發表、主持會議、議程檢討，此些方面皆順利達成任務。

二、過程

第 223 屆電化學國際研討會 在多倫多凱悅飯店之會議中心舉行, 今年會議涵蓋 44 個主題, 發表之技術論文有 1,514 篇，去年則有 1,653 篇，參加會議論文數相差不多，表示此一會議已爲穩定之會議，對此些研究領域之學者已將此一會議視爲例行之交換研究心得之重要會議。此一研討會涵蓋全球領先之(A) 奈米技術之主題 (Nanotechnology General Topic), (B) 能源技術:電池、燃料電池與能源轉換(Energy Technology: Batteries, Fuel Cells and Energy Conversion) (B1-B9), (C) 有機電化學新介電材料之研發(Inovations and New Dielectrics in Organic Electrochemistry), (D) 腐蝕, 保護層與陽極層(Corrosion, passivation, and Anodic Films) (D1, D2), (E) 介電層與半導體材料, 元件與製程(dielectric and semiconductor materials, device, and processing) (E1-E9), (F) 電化學/化學沉積與蝕刻(Electrochemical/chemical deposition and etching) (F1, F2), (G) 電化學合成與工程(Electrochemical synthesis and engineering) (G1-G4), (H) 奈米管與奈米結構

(Nanotubes and Carbon nanostructures) (H1-H9), (I) 電化學之物理與分析(Physical and Analytical Electrochemistry)(I2-I6), and (J) 感測器與顯示器:理論, 材料與製程 (Sensors and Displays: Principles, materials and processing) (J1-J3)。每一主題細分多項子題, 從以上之子項可看出重點領域。!! 電化學國際研討會歷史悠久目前已舉辦過 223 屆，若以每年舉辦兩次會議計算，此一會議至今已舉辦第 112 年了。關於電化學研討會，近幾年來筆者每年皆參加，從初次參加時對此一研討會之一知半解，至今對常常參加會議的學者、領域、及徵稿模式可說是完全了解與掌握，且目前本人亦擔任此一會議之 E9“寬能隙半導體材料與元件”之議程委員。

此一會議在兩年前才於加拿大魁北克省之蒙特利舉行之 ECS 春季會議；去年此一時間在美國西雅圖舉行，今年之會議時間又到了!!每年兩次之 ECS 會議(分春季與秋季)，第 223 ECS meeting 今年於 5 月 12 日開始, 會議地點又到加拿大舉行，不過此次會議是在安大略省多倫多舉行。由於每年固定參加春季會議，今年不僅參加會議，並且繼續擔任會議議程成員(program committee member)，負責規劃議程時間，邀請演講，論文審稿，並協助出版會議論文之書籍等會務。本次應大會邀請，不僅擔任一場會議的主持人，亦發表三場口頭論文演講及一場看板海報發表。另外, 亦聆聽國外學者之最新研究成果，與同一領域之教授進行研究心得分享。另一方面，於會議期間認識不少美國、加拿大、愛爾蘭、大陸等之年輕研究學者，互相交換研究心得，此次應該有機會可展開實質之國際合作。

今年筆者亦如往年參與之主題爲(E) 介電層與半導體材料, 元件與製程 (dielectric and semicoductor materials, device, and processing)其中 E9 寬能隙半導體材料與元件(Wide Bandgap Semiconductor Materials and Device)外,今年又擴展至參加 E2 石墨烯, 鍺/三五, 重要材料在互補式金氧半元件之應用(Graphene, Ge/III-V, and Emergying materials for post CMOS Applications)。關於 E9 此一 section 主要討論寬能隙元件與材料, 包括氮化鎵(GaN),氧化鋅(ZnO), 不僅如此, 亦包括發光二極體(LED), 感測器(sensor)等元件，今年較熱門之主題爲於製作 GaN 之 Power device, 電晶體與其在生醫之應用，GaN 材料缺陷之研究，與討論如何降低，與氧化鋅(ZnO), 氧化鎵(GaO), 氧化鋅銦鎵(IGZO)研製程透明電晶體或應用於加強光電元件之效率之應用之論文發表。關於 E2 之部分主要探討最新之石墨烯之研究, 今年已不再只是探討如何備製石墨烯，已開始討論如何將其應用在電晶體、

感測器、軟性顯示器；更重要的爲石墨烯原來是無能隙之材料，現今美國之學者已了解此一現象, 開始研究如何製造出具能隙之石墨烯，下一步將挑戰製作 n-type 與 p-type 石墨烯，屆時將會再掀起一波石墨烯熱潮。

由於會議範圍涵蓋內容太廣泛, 除寬能隙外, III-V 化合物亦爲本人有興趣之領域, 今年此一會議之另一重點在討論 x-ray 之感測器。由於 x-ray 之功能強大, 近年來 x-ray 在各方面之應用大爲廣泛，有應用於安全檢查，有應用於生醫檢測，早期之 x-ray 感測器多利用材料將 x-ray 轉換成可見光並產生光電流，然此一作法量子轉換效率太低，目前已改爲研製厚的直接能隙材料，直接將 x-ray 轉換成電子-電動對之光電流，如此一來即可改善轉換率之問題。

此外, 筆者有幸受邀爲 Wide Bandgap Semiconductor Material and Device 之兩場演講， 演講題目分別爲”InGaN LEDs Grown on Patterned Sapphire Substrates with Modified Top-Tip Cone Shapes”與”Growth and characterization of single crystalline Ga-doped ZnO thin films using MOCVD ”，由於現今 LED 特別是高功率發光二極體仍存在內部量子效率太低之問題，其主要原因爲 GaN 磊晶成長在藍寶石基板上存在 16%晶格不匹配之問題，雖然已有多種解決方法, 如以圖案劃藍寶石爲磊晶之基板, 或橫向磊晶技術, 及奈米圖案基板之技術, 本論文提出另一更具改善之作法，結合乾式與濕式之蝕刻製作出頂端經過修飾之圖案劃藍寶石基板，如此一來，不僅可降低材料缺陷, 更有助於發光二極體之取光, 且製作成本低廉。

筆者進行第一場演講

另一篇演講爲以 MOCVD 成長 GaZnO, 發現加入 Ga 至 ZnO 可提供成膜之 GZO， 且其可與 p-GaN 形成歐姆接觸，如此一來其即可取代目前廣泛使用可是具毒性且價格高昂之 ITO 透明導電膜，採用 GZO 當透明導電膜亦可維持發光二極體之電性，更可提供發光二極體之高效率與高功率之工作特性，本論文提出以 GZO 取代 ITO 之可行性評估，會議報告後，引起參加會議之學者熱烈討論，不僅對報告內容交換心得，更是對本實驗室之研究能量與技術大加讚賞，並提出未來合作之規劃。此外本論文已撰寫投稿於 Optical Express 並進行審稿中。

筆者進行第二場演講

此外,另一場演講爲“Effect of Different Patterned Epilayers on Lift-Off Process by Finite Element Simulation”，此一論文之重點爲提出一製程可解決目前紅光高亮度但高製作成本之問題,提出以濕式蝕刻法配合側向移除犧牲層之作法將磊晶基板保留下來，可重複使用，會議中提出以模擬方式評估爲何此以做法在製程中會發生磊晶膜破裂之現象，並提出解決之道。報告結束後，美國紐約州立大學 University at Albany 教授”Serge Oktyabrsky”與我討論，並提出經驗分享，一語道破技術核心，提出更簡易方式，其將犧牲層先進行氧化，而後再蝕刻，Serge

Oktyabrsky 教授表示如此一來不僅分離率快速，且可解決論文中欲解決之問題，若真如此，我想此次會議最大之收穫及爲此一關鍵技術。

筆者與學生在會場合影

三、心得

電化學國際研討會雖然涵蓋領域很多，然寬能隙半導體仍是領域中重要一主軸，筆者近幾年來幾乎每次皆參加，且投稿之論文數量越來越多，已引起大會之注意，不僅協助論文審稿，此次更應邀爲主持會議與邀請演講，研討會之委員會更主動邀請筆者參與第 222-225 屆電化學國際研討會之會議規劃與主持研討會進行，本人已正式成爲會議之委員會成員之一。由此可知欲投入一重要國際協會與研討會，“持續深耕”是一重要之方法，如此一來將可逐漸扮演一重要之影響力。

此次之重要收穫爲與國際上從事氧化物或氮化鎵研究之學者互相交換心得且此次又跨入另一領域，又認識新領域之研究學者,其對目前我們從事之化學分立技術提出及有效之建議，希望回臺後再加以測試確認其建議之可行性，此外透

過論文發表, 也讓國外公司之研究學者對中興大學光電元件之研究留下深刻印象, 未來合作機會頗大 !!

另一方面, 在會議中有收到加拿大國家研究室 NRC 之對外服務之廣宣, NRC 是加拿大很重要之國家實驗室, 此一實驗室內有大型設備與相當多之研究人員, 此一廣宣頗類似目前國科會所爲小聯盟之作法, 因筆者之單位目前也參與小聯盟計畫, 希望透過此一廣宣可做爲我們小聯盟業務推廣之參考。

四、建議

由於臺灣出席此會議者人數眾多，然大多個別前往，目前國科會光電學門已成立一網站，公告參加研討會之學生，讓學生有機會以組團之方式前往，目前之效果據說不錯，如此一來不僅可促進教授間之學術交往，亦可發揮對大會之影響力。

多次參與研討會, 目前發現學生出國機會越來越頻繁，不知是否如此，讓學生反而不知珍惜，往往於研討會期間只有貼海報或口頭報告時才出現，如何建立一機制，讓學生可於會議中多聽聽與會者其他人之報告，或國外學者進行經驗分享，方不辜負政府以納稅人之費用補助學生出國之美意。

此次會議另一作法亦值得國內舉辦研討會效法；及論文摘要置於雲端硬碟，供有需要者自行下載，主要目的爲目前智慧型手機大爲普及, 若自行下載, 不僅無攜帶之問題, 亦備於查詢與保存, 更符合環保之概念。

五、攜回資料

此次會議帶回一本第 223 屆電化學國際研討會會議議程,E9 transection on 之書籍, 展覽廠商介紹。

六、附件: 發表之論文

InGaN LEDs grown on patterned sapphire substrates with modified top-tip cone shapes

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Abstract

High efficiency GaN-based light-emitting diodes (LEDs) are used in a large range of potential applications such as full-color displays, traffic signals, automobiles, solid-state lighting, backlights of liquid-crystal displays, and so on. High luminescence efficiency is needed in LEDs devices used for these applications. However, it is well known that a high threading dislocation density (typically 10^9-10^{11} cm^{-2}) is inherent in the GaN epilayer on lattice-mismatched substrates consisting of sapphire and silicon carbide [1]. High dislocation density would affect the device characteristics including device lifetime, electron mobility, and the quantum efficiency of radiative recombination.

Recently, various growth techniques, such as epitaxial lateral overgrowth (ELOG), pendeo-epitaxy and facet-controlled epitaxial lateral overgrowth, have been proposed to reduce the threading dislocation density in GaN epilayer to the range of 10^6-$10^7 cm^{-2}$. Furthermore, because of its single-growth process with no interruption, patterned sapphire substrate (PSS) technique is another promising method to achieve the high quality GaN epilayers. Nevertheless, the PSS technique requires a long time to merge the epilayer grown on etched and non-etched sapphire substrate, and then reaches a smooth film surface. According to the past research [2], the InGaN/GaN film with a high quality can be obtained by metal organic chemical vapor deposition (MOCVD) on the cone-shape PSS. For the growth on cone-shape PSS, the epilayer is merely grown on the flat basal of sapphire in the first stage. In addition, there exists

no preferential orientation for the epilayer growth on cone areas. This indicates the less growth time for epilayer with a smooth film surface on cone-shape PSS can be obtained than that on a conventional PSS.

In this study, the cone-shape PSSs have been fabricated for the growth of InGaN LED structures. Moreover, the modified top-tip shapes in the PSSs were formed by the wet chemical etching with various treatment times. The GaN growth modes, film quality and LED performance were investigated for growth on a series of PSSs.

The cone-shape PSSs were fabricated on (0001) sapphires by using an inductively coupled plasma reactive ion etching (ICP-RIE) system using the reactive Cl_2 gas. The diameter, interval and height of each cone-shape pattern were 2.4 μm, 0.5 μm and 1.5 μm, respectively. After the ICP-RIE process, the fabricated cone-shape PSSs were etched with a mixture of H_2SO_4:H_3PO_4 (3:1) solution at 250 °C for 3-10 min to form the various top-tip shapes. The LED structures consisted of a undoped GaN, a n-type GaN:Si, an InGaN/GaN multiple quantum well (MQW) active region and a p-type GaN:Mg layer were grown on these PSSs in sequence by MOCVD. For the device process, a mesa pattern of LED sample was defined with the size of 24 × 45 $mil.^2$.

Fig. 1 shows the scanning electron microscope (SEM) images of cone-shape PSSs with various wet etching times of 3, 5, 7 and 10 min, respectively. It was found that the top-tip shape was transformed from smooth to angular with increasing the wet etching time. Moreover, the bottom size of each cone-shape was enlarged and the interval was reduced as the wet etching time was increased, which leaded to the decrease in c-plane ratio of sapphire.

Fig. 2 demonstrates the light output power as a function of injection current for the LEDs grown on cone-shape PSSs with and without wet etching, respectively. It revealed that the light output of LED device was improved as the PSS was treated with wet etching, which resulted from the improvement in epilayer quality due to the reduction in c-plane ratio of sapphire. However, as the etching time was more than 3 min, the light output was decreased slightly. This could be attributed to the epilayer growth not only on the c-plane area but also on the angular cone region in the initial stage as the wet etching time was increased. It caused the higher dislocation density in epilayer and the deterioration in device performance.

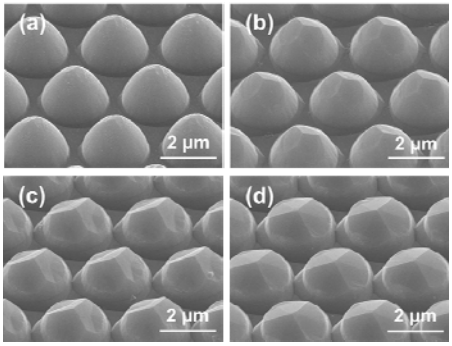

Fig. 1 SEM images of PSSs with various wet etching times of (a) 3 min, (b) 5min, (c) 7 min and (d) 10 min.

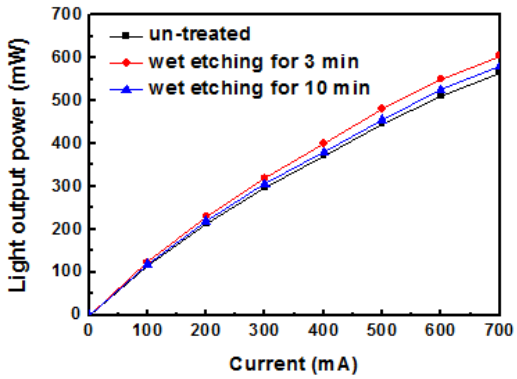

Fig. 2 Light output power as a function of injection current for the LEDs grown on cone-shape PSSs with and without wet etching.

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Growth and characterization of single crystalline Ga-doped ZnO thin films using metal-organic chemical vapor deposition

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Abstract

Ga-doped ZnO (GZO) thin films with high thermal stability and high carrier mobility are essential to develop transparent conductive electrodes (TCEs). In this study, the carrier concentration and the electrical resistivity of GZO thin films are related to the Ga flow rates. GZO thin films have been grown on c-plane sapphire substrates with Ga doping concentration of 10^{20} cm^{-3} using metal-organic chemical vapor deposition technique. Crystalline structures of as-grown and post-annealed samples are studied by x-ray diffraction technique. Their transparency is also tracked by n & k analyzer. Under optimized growth parameters, the lowest resistivity of GZO is 5.5×10^{-4} ohm-cm.

Keywords: Ga-doped ZnO, MOCVD, resistivity

Introduction

Transparent conductive oxides (TCOs) attract considerable attention due to their extensive applications in flat panel displays, light-emitting diodes, solar cells, touch panels, and photodiodes[1,2]. Among the various TCOs, tin-doped indium oxide (ITO) thin films have been widely used in display applications because of their low resistivity (10^{-4} Ω-cm) and high transparency (88 %) in the visible region [3]. But, thermal stability of ITO is poor for optoelectronic devices[4]. In addition, indium is an expensive element. Therefore, many studies are focused to find suitable substitute(s) for ITO. Recently, various TCOs materials such as ZnO, SnO_2, and TiO_2 have been introduced as replacements for ITO. ZnO thin films are one of the candidates for a replacement with ITO, for their low costs and easy fabrications.

ZnO thin films show high potential as TCOs especially when they are doped with group III elements such as Al, In, Ga [5-8]. Among these metal dopants, Ga is found to be more attractive for its covalent bond length of Ga-O (0.192 nm) which is slightly smaller than that of Zn-O (0.197 nm). Therefore, even high Ga doping concentration does not make considerable deformation in ZnO lattice structure. Furthermore, Ga has lower cost than In and has higher oxidation resistance than Al, which makes it as a preferred dopant for ZnO thin films in TCO applications. Ga doped ZnO (GZO) are reported as n-type thin films [9-10]. GZO can be deposited by various methods such as sputtering, thermal evaporation, pulsed laser, sol-gel, spray-pyrolysis, and chemical vapor deposition [11-17]. In this work we present GZO thin films grown by metal-organic chemical vapor deposition (MOCVD) technique, which is very important in mass production and also multilayer technology. GZO thin films with different Ga-doping concentrations are deposited on (0001) sapphire substrates. Effect of post-annealing on the structural, electrical, and optical properties of GZO thin films are investigated.

Experimental procedure

Thin films are grown on (0001) sapphire substrates using a modified Emcore D-180 MOCVD system. Diethylzinc (DEZn), purified oxygen (99.999%) and triethylgallium (TEGa) were used as Zn precursor, oxidizer, and Ga precursor, respectively. Purified Ar (99.999%) is used as carrier gas, passing through the DEZn and TEGa bubblers to deliver the DEZn and TEGa vapors to the reactor. Two sets of deposition are completed. In first set, the flow rates of DEZn and oxygen were fixed at 100 and 160 sccm, respectively. TEGa flow rate was tuned from 5 to 20 sccm at 350 °C for 15 minutes. In second set, the flow rates of DEZn, oxygen, and TEGa were fixed at 100, 160, and 10 sccm, respectively. Depositions are completed at 350 °C at different times for 10, 12, and 15 minutes.

Some of the as-grown thin films of two sets are undergone a rapid post-annealing at 550 °C for 2 minutes in N_2 environment. Crystalline quality of thin films are measured using a high resolution x-ray diffraction (HR-XRD) system (PANanalytical, X'Pert Pro MRD) with a Cu Kα line (λ = 1.541874) as the radiation source, and Ge (220) as the monochromator. An n & k analyzer is employed to measure the optical transmittance and thickness of samples. Resistivity, and impurity concentration of samples are measured by of Hall measuring system and electronic mobility.

Results and discussion

Figure 1 (a) displays typical XRD patterns of as-grown thin films grown for 15 minutes at different Ga precursor flow rates. XRD peak for the sample grown under Ga precursor flow rate of 5 sccm, shows the diffraction peak corresponding to (002) and (101) ZnO, and indicating no significant Ga incorporation. However, increasing the Ga precursor flow rate to 10, 15, and 20 sccm, decreases the (002) direction of crystallinity and attributed to ZnO.

XRD peaks related to GZO thin films grown under a fixed Ga precursor flow rate (10 sccm) for 10, 12, and 15 minutes are displayed in Figure 1(b). All samples show almost the same structures including (002) and (101) ZnO.

The XRD patterns related to GZO samples in Figure 1(a) and (b) after post-annealing at 550 °C in N_2 environment for 2 minutes are displayed in Figure 1(c) and (d). It is revealed that annealing has no effects on the crystalline structures of all of the as-grown

samples

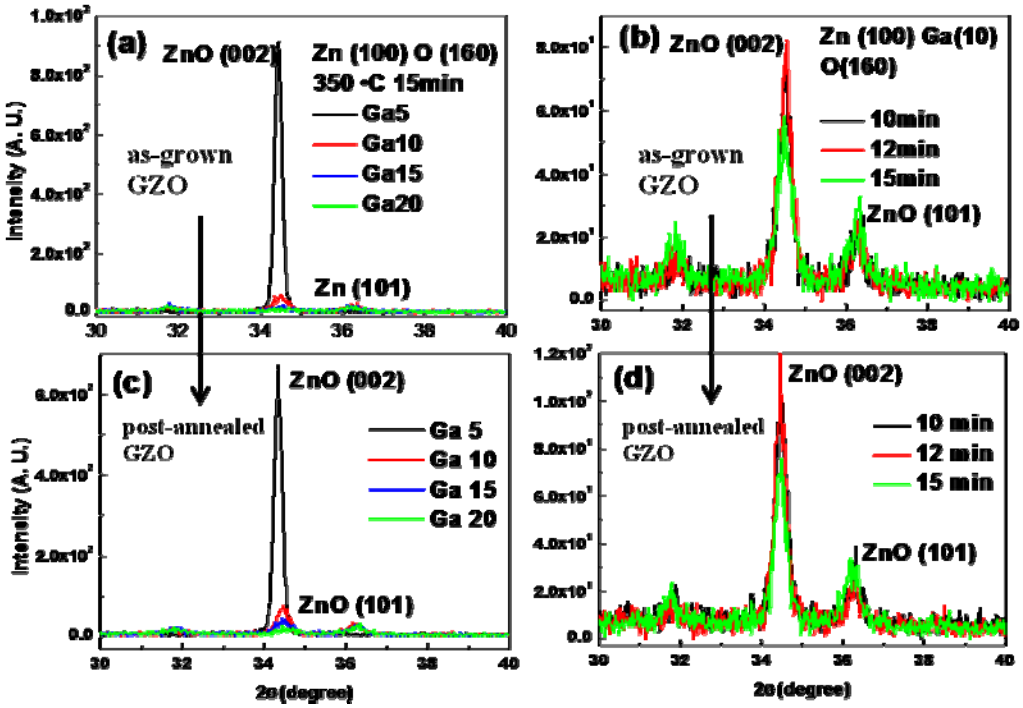

Figure 1. XRD patterns of GZO thin films grown at (a) different Ga precursor flow rates, (b) different growth time, (c) and (d) XRD patterns of GZO thin films in (a) and (b) after post-annealing under N_2 flow for 2 minutes.

Figure 2 (a-d) respectively show the transmittance spectra in the range of 200 to 1000 nm for GZO thin films in Figure 1 (a-d). All GZO thin films show the average

transmittance above the 90%. Such high transmittivity is very important in optoelectronic devices.

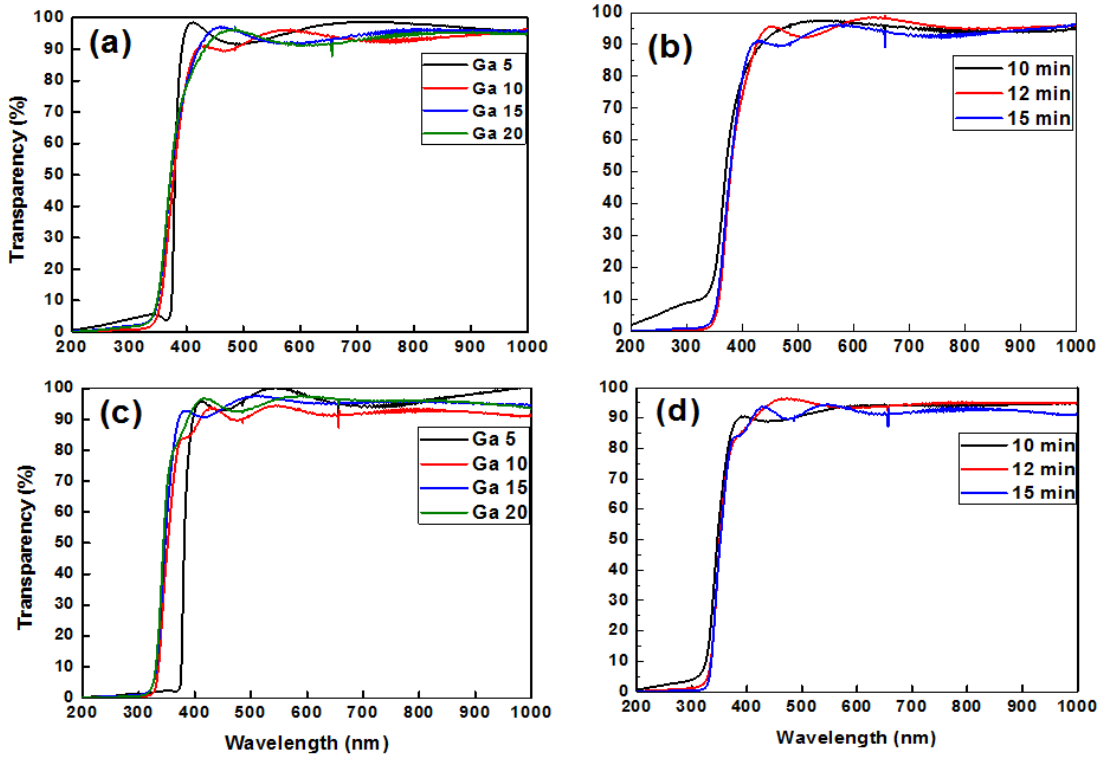

Figure 2. Optical transmission spectra of GZO thin films grown at (a) different Ga precursor flow rates, (b) different growth times. (c) and (d) Optical transmission spectra of GZO thin films in (a) and (b) after post-annealing under N_2 flow for 2 minutes.

Figure 3 (a) displays resistivities of post-annealed GZO thin films grown under different Ga precursor flow rates. Higher Ga precursor flow rates result to greater resistivities (~ 7.25×10^{-4} ohm-cm for 20 sccm flow rate). It could be due to the high Ga precursor flow rate not contributing to the Ga concentration, but resulting in the ZnO lattice deformation. Figure 3 (b) shows resistivities of post-annealed GZO thin films grown at different times. Post-annealed sample grown for 12 minutes shows the highest resistivity (~ 7×10^{-4} ohm-cm) and that grown for 15 minutes reveals the lowest resistivity (~ 5.5×10^{-4} ohm-cm). As the GZO thin films grown at longer time,

the thickness will increase. It will contribute to more Ga dopant concentration after the post-annealed GZO for thicker GZO thin films.

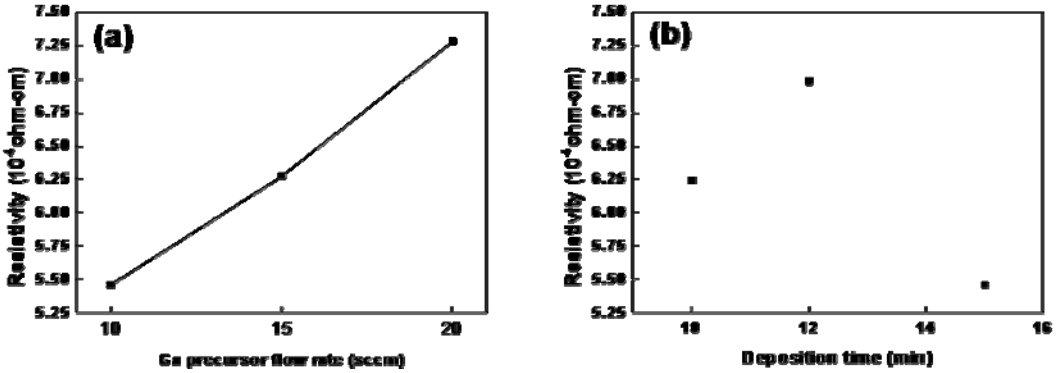

Figure 3. The resistivity of post-annealed GZO thin films under different (a) Ga flux rate and (b) deposition times.

Conclusion

GZO thin films are grown by an MOCVD technique under different deposition conditions. Then, some of the samples are annealed for 2 minutes under N_2 environment. X-ray patterns does not reveal any corporation of Ga in the GZO structures. Moreover, x-ray measurement does not show any change in the crystallinities GZO thin films after post-annealing. All the as-grown and post annealed samples show a relatively high transmittivity (over 90 %), which is important in optoelectronic technology. In terms of resistivity, post-annealed samples with higher initial Ga flow rate show higher resistivities, but overall resistivity is still quite low (~ 5.5 to 7.3) × 10^{-4} ohm-cm.

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