國家同步輻射研究中心

出國心得報告書

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出國日期：2019/12/16 - 2019/12/21

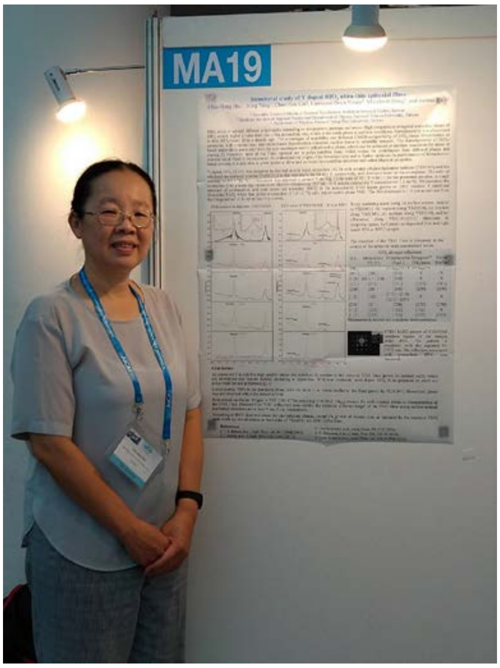
目的地(國家、城市)：新加坡

參加會議名稱：第 16 屆亞洲結晶學會議

一、 參加會議經過

16th Conference of the Asian Crystallographic Association (2019 AsCA)於 2019 年 12 月 17-20 日假國立新加坡大學(National University of Singapore)舉行，中心同仁分批前往，本人一行於 12 月 16 日上午出發，20 日傍晚參加閉幕典禮後於 21 日返台。

此次會議總計有來自以亞洲、大洋洲學者及學生為主的近 500 位與會者，此外亦有約 50 位來自歐洲與美洲的學者。根據大會資料韓國和印度有 60 多位與會者，中國大陸加香港和地主國新加坡各有 50 多位與會者，日本則為最多與會人員的國家。台灣則有本中心同仁加上來自其他單位如中研院、台大、清大、師大、暨南大學等教授學者，有近 30 人員參加。大會也特別報告與會者當中約有 1/3 為女性。這次會議總計有約 250 篇海報發表，另有 170 多個口頭報告。本人於會議中有一份海報展示(詳圖一)，與國外學者討論交流。



圖一、報告人與展示的壁報合影

此次參加會議除了個人報告設施發展近況或研究結果，另一目標是爭取 2022 AsCA

主辦權。除了中心代表台灣爭取之外，另外韓國也爭取在濟州島辦理。兩國代表於 12 月 18 日於 AsCA Committee Meeting 中提出規劃報告，除了議程、會場、交通、住宿、飲食、報名費等細節外，值得注意的是有 committee 委員詢問 organizing committee 中女性成員的比例，此議題近年數次在國際會議中被提起，可做為未來籌備爭取主辦國際會議時的考量點之一。大會於 19 日由各國代表投票決定 2022 主辦國，很遺憾由韓國取得主辦權。

此次會議主題可分成 3 部分 第一為大分子(macromolecular crystallography)與生物結構為最大宗，其二為化學結晶學(Chemical Crystallography)，第三為材料與應用(Materials and Applications)。三位大會 plenary speakers 一位是來自韓國 Korea Research Institute of Bioscience and 的 Dr. Myunghee Kim 報告為微生物引起疾病的機制及後續之免疫調整的角色探討;另兩位都是化學晶體學，分別是 metal-organic frameworks (MOFs)和 covalent-organic frameworks (COFs)領域的知名學者，分別是 Kyoto University, Institute for Advanced Study 的 Prof. Susumu Kitagawa **和** National University of Singapore, Department of Chemistry 的 Prof, Donglin Jiang，他們利用簡單的化學結構建置成結構複雜的 2D 或 3D 的孔洞性結構，由結構的設計到功能性的應用，好似在堆積木，讓我們這些外行人歎為觀止。實驗設施和設備的發展大致被歸類在第三個主題，此領域的與會者相對較少。此行了解目前國際上結晶學相關研究的趨勢，獲益良多。

二、 與會心得

此次會議於第一天下午安排一個半小時，分 3 個領域平行進行 Flash presentations by students/early career researchers。參加對象為有海報展出的32歲以下的學生、博後或年輕學者，每位報告人利用3分鐘的時間用一張投影片說明海報的重點，時間控制、科學概念及報告的清晰度是評審的評分重點，這種報告對報告人是一很好的訓練，在很短的時間內報告重點，吸引觀眾的注意；而對觀眾而言，可以很方便快速瞭解報告主題內容，作為進一步觀看海報討論的選擇，值得未來辦理會議時參考嘗試。較遺憾的是在此次48位參加者中沒有來自台灣的與會者參加此項 Flash presentation，可能因為此次參加者多為較資深的學者和研究人員。

三、 建議

值得注意的是近年來發展迅速的 cryoEM，其實驗方法和研究結果在約20個 microsymposium 中即佔2個，吸引許多聽眾。報告中可看出實驗技術仍在快速發展，幾個報告人都是來自規模可觀的顯微術中心，結合樣品製作、熟悉各種電子顯微鏡的操作模式的技術人員，以及數據模擬等不同專長的研究人員和科學家共同組成團隊合作，目前尚未達到 routine operation 的階段，國內應集中人力物力建立一顯微術中心，或是較理想且具有競爭力的做法。

四、 附件

Poster MA19摘要

Abstract for AsCA 2019　K. Materials and Polymer

SG-ASCA1392 Structural study of Y doped HfO2 ultra-thin epitaxial films

Chia-Hung Hsu, Song Yang, Chun-Yen Lin, Lawrence Boyu Young, Minghwei Hong, and Jueinai Kwo

HfO_2-based materials have been extensively studied and are considered as leading replacements of SiO_2 for gate insulator applications in CMOS technology because of its high dielectric constant and suitable band gap offset with Si. Depending on temperature, pressure and stress, HfO_2 exists in several different polymorphs. High temperature tetragonal and cubic phases of HfO_2 exhibit higher *k* value than that of the monoclinic one, which is the stable phase at ambient conditions. Various elements, such as Y and La, have been successfully doped into HfO_2 to stabilize the metastable cubic phases and achieved a high *k* value.[1,2] Ferroelectricity was discovered in thin HfO_2-based films a decade ago. The advantages of scalability and Si-based CMOS-compatibility of HfO_2-based ferroelectrics as compared with conventional perovskite-based ferroelectrics stimulate another boom in scientific research. The ferroelectricity of HfO_2-based materials is associated with the non-centrosymmetric orthorhombic phase, which can be achieved at ambient conditions by stress or doping.[3] However, most of the films reported are in polycrystalline form, which makes the contribution from different phases and orientations difficult to be separated. To understand the origin of its ferroelectricity and to further optimize the performance of ferroelectric-based devices, it is desirable to grow epitaxial films and correlate its crystalline structure with other physical properties.

It is a challenging task to determine the crystalline structure of HfO_2-based thin films, because of the structural similarities between different phases and possible coexistence of polymorphs and crystalline orientations, in additional to the ultra-thin sample thickness, a few tens of nanometers, to comply with the application requirements. In this work, we reported the structural properties of ~15 nm thick Y-doped HfO_2 epitaxial films investigated by using X-ray scattering. Y-doped HfO_2 was prepared by thermal atomic layer deposition (ALD) with tetrakis ethylmethylamino hafnium (TEMAH) and tris ethylcyclopentadienyl yttrium ($Y(EtCp)_3$) as the precursors for Hf and Y, respectively, and deionized water as the co-reactant. The ratio of reaction cycles of the two components was adjusted to control Y doping. No additional thermal treatment is necessary to obtain crystalline films. All the samples exhibit epitxial growth and no monoclinic phase was observed. Thermal annealing up to 800°C does not cause obvious change in the crystalline structure. The structure of films of different Y doping grown on YSZ substrates of various orientations will be presented.

References

1. Z. K. Yang, et al, Appl. Phys. Lett. **90**, 152908 (2007).
2. Z. K. Yang, et al, Appl. Phys. Lett. **91**, 202909 (2007).
3. T. S. Böscke, et al., Appl. Phys. Lett., 99, 102903 (2011).

Structural study of Y doped HfO_2 ultra-thin epitaxial films

Chia-Hung Hsu[1], Song Yang[1], Chun-Yen Lin[1], Lawrence Boyu Young[2], Minghwei Hong[2], and Jueinai Kwo[3]

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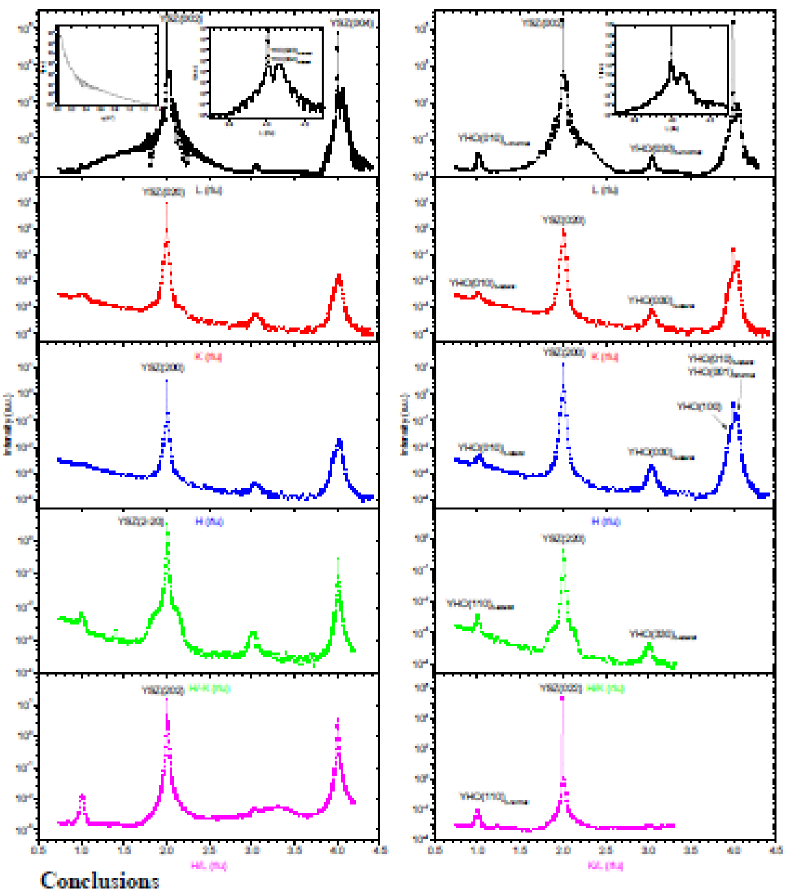
HfO_2 exists in several different polymorphs depending on temperature, pressure and stress. High temperature tetragonal and cubic phases of HfO_2 exhibit higher *k* value than that of the monoclinic one, which is the stable phase at ambient conditions. Ferroelectricity was discovered in thin HfO_2-based films a decade ago. The advantages of scalability and Si-based CMOS-compatibility of HfO_2-based ferroelectrics as compared with conventional perovskite-based ferroelectrics stimulate another boom in scientific research. The ferroelectricity of HfO_2-based materials is associated with the non-centrosymmetric orthorhombic phase, which can be achieved at ambient conditions by stress or doping.[1] However, most of the films reported are in polycrystalline form, which makes the contribution from different phases and orientations difficult to be separated. To understand the origin of its ferroelectricity and to further optimize the performance of ferroelectric-based devices, it is desirable to grow epitaxial films and correlate its crystalline structure with other physical properties.

Y-doped HfO_2 (YHO) was prepared by thermal atomic layer deposition (ALD) with tetrakis ethylmethylamino hafnium (TEMAH) and tris ethylcyclopentadienyl yttrium ($Y(EtCp)_3$) as the precursors for Hf and Y, respectively, and *deionized* water as the co-reactant. The ratio of reaction cycles of the two components was adjusted to control Y doping. Cycle ratio of Hf : Y = 16 : 1 for the presented samples. A rough estimation from a scanning transmission electron microscopy (STEM) EDX results yielded the Y concentration 3.2 mol%. We presented the structure of as-deposited and post deposition annealed (800°C in He atmosphere) YHO layers grown on (001) oriented Y stabilized Zirconia (YSZ), which has lattice mismatches of 1.5~-1.7% with orthorhombic phase YHO. The film thickness is ~16 nm as derived from the fringe period of X-ray reflectivity curves.

XRD scans of as-deposited YHO/YSZ(001) XRD scans of YHO/YSZ(001) RTA at 800°C

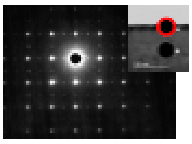


X-ray scattering scans along (a) surface normal parallel to YSZ(001), (b) in-plane along YSZ(010), (c) in-plane along YSZ(100), (d) in-plane along YSZ(110), and (e) off-normal along YSZ(101)/(011) directions in reciprocal space. Left panel: as-deposited film and right panel: RTA at 800°C sample.

The structure of the YHO films is discussed in the context of the selection rules summarized below.

HfO$_2$ allowed reflections				
S.G. {*hkl*}	Monoclinic ($P2_1/C$)	Orthorhombic ($Pca2_1$) $a > a_{YSZ} > c \sim b$	Tetragonal* ($P4_2/nmc$) $c > a_{YSZ} > a$	Cubic ($Fm\bar{3}m$)
{001}	(100)	(010)	X	X
{110}	(011)、(110)	(110)	X	X
{111}	{111}	{111}	{111}	{111}
{200}	{200}	{200}	{200}	{200}
{102}	{102}	(012)、(210) (120)、(201)	X	X
{220}	{220}	{220}	{220}	{220}
{112}	{112}	{112}	(112)	X
{113}	{113}	{113}	{113}	{113}

*Represented in doubled cell to facilitate direct comparison.



STEM SAED pattern of YHO/YSZ interface region of the sample under RTA. The pattern is consistent with the reported O-HYO one. No reflection associated with monoclinic HYO was observed.

Conclusions

As-deposited film exhibits high quality crystalline structure, in contrast to the reported YHO films grown by thermal ALD, which are amorphous and require thermal annealing to crystallize. With heat treatment, most doped HfO_2 films prepared by ALD are polycrystalline and polyphasic.[2-3]

Orthorhombic YHO is the dominant phase, with the short b- or c-axis similar to the films grown by PLD.[4-5] Monoclinic phase was not observed within the detection limit.

Pronounced oscillation fringes in YSZ (00*l*) CTRs persisting over ±0.5 rlu_{YSZ} reveals the well oriented epitaxial characteristics of the YHO films. Derived from YHO diffraction peak widths, the structural coherent length of the YHO films along surface normal and lateral directions are at least 9 and 5 nm, respectively.

Annealing at 800°C does not cause obvious structure change, except the growth of domain size, as indicated by the narrower YHO peak width and the shoulders on both sides of YSZ(400) and (040) reflections.

References

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2. J. Müller, et al., J. Appl. Phys. **110**, 114113 (2011).
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