

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 29-03-2010		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 3-Jul-2007 - 2-Apr-2008	
4. TITLE AND SUBTITLE Photo-activated synthesis of functional oxide thin films			5a. CONTRACT NUMBER W911NF-07-1-0467		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Shriram Ramanathan			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Harvard University Office of Sponsored Research 1350 Massachusetts Ave. Holyoke 727 Cambridge, MA 02138 -			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 53057-MS-II.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We report on the effect of ultra-violet (UV) irradiation on structural and interfacial phenomena in thin film pure and doped zirconia grown by physical vapor deposition. Interfacial layer formation by substrate oxidation and resultant densification of zirconia layer was found in yttria doped zirconia (YDZ) films grown on Si, while no change was observed in identical films grown on Ge. A comparison of un-doped zirconia and YDZ films indicates yttria doping significantly assists the structural changes during UV irradiation.					
15. SUBJECT TERMS oxides, synthesis, materials science					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Shriram Ramanathan
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 617-496-0358

Report Title

Photo-activated synthesis of functional oxide thin films

ABSTRACT

We report on the effect of ultra-violet (UV) irradiation on structural and interfacial phenomena in thin film pure and doped zirconia grown by physical vapor deposition. Interfacial layer formation by substrate oxidation and resultant densification of zirconia layer was found in yttria doped zirconia (YDZ) films grown on Si, while no change was observed in identical films grown on Ge. A comparison of un-doped zirconia and YDZ films indicates yttria doping significantly assists the structural changes during UV irradiation. Interestingly, the effect of UV photons becomes minimal at ~300 oC in films grown on Si, while the effect of UV becomes more pronounced in YDZ films grown on Ge. An interfacial layer was formed between YDZ and Ge substrate at 300 oC in presence of UV irradiation, in contrast to the sharp interface maintained even after annealing at 300 oC without UV. Those results suggest that photon irradiation may be an elegant approach to tailor structural and interfacial properties at near-atomic length scales.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

An investigation into photon irradiation induced structural and interfacial phenomena in pure and alio-valently doped zirconia thin films, M. Tsuchiya and S. Ramanathan, Philosophical Magazine, 88, 2519 (2008)

Photon-assisted oxidation and oxide synthesis: A review, M. Tsuchiya, K.R.S.S. Sankaranarayanan and S. Ramanathan, Progress in Materials Science, 54, 981 (2009)

Number of Papers published in peer-reviewed journals: 1.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Masaru Tsuchiya	0.25
FTE Equivalent:	0.25
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Masaru Tsuchiya
Total Number: 1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Photo-activated synthesis of functional oxide thin films

PI: Shriram Ramanathan

Harvard School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA

Abstract

We report on the effect of ultra-violet (UV) irradiation on structural and interfacial phenomena in thin film pure and doped zirconia grown by physical vapor deposition. Interfacial layer formation by substrate oxidation and resultant densification of zirconia layer was found in yttria doped zirconia (YDZ) films grown on Si, while no change was observed in identical films grown on Ge. A comparison of un-doped zirconia and YDZ films indicates yttria doping significantly assists the structural changes during UV irradiation. Interestingly, the effect of UV photons becomes minimal at $\sim 300^\circ\text{C}$ in films grown on Si, while the effect of UV becomes more pronounced in YDZ films grown on Ge. An interfacial layer was formed between YDZ and Ge substrate at 300°C in presence of UV irradiation, in contrast to the sharp interface maintained even after annealing at 300°C without UV. Those results suggest that photon irradiation may be an elegant approach to tailor structural and interfacial properties at near-atomic length scales.

1. Introduction

Zirconia (ZrO_2) is a technologically important material owing to its various applications as refractory material, thermal barrier coatings and oxygen sensors.[1] Besides applications of bulk zirconia, ultra-thin film zirconia (< 100 nm) is of great interest in recent years as high dielectric constant gate insulators for metal-oxide-semiconductor (MOS) transistors,[2][3] and electrolyte for intermediate temperature solid oxide fuel cells.[4][5] Due to difficulty in controlling the crystalline phase in undoped zirconia, aliovalent doping (such as Y^{3+}) is commonly employed to stabilize the cubic phase.[6] Doping of aliovalent cations creates charge-compensating oxygen vacancies, introducing changes in electrical and electrochemical properties. For example, an increase in vacancy concentration enhances oxygen-ion conduction, thereby aliovalent doping is an attractive option for applications in solid state ionic devices,[7] while charge trapping and ion-drift of oxygen vacancies can affect the reliability of electronic devices.[8] In addition, phase stability and microstructure evolution in thin film zirconia are sensitive to oxygen vacancy concentration.[9] Therefore, a detailed understanding and control of oxygen point defects and interfaces in thin film zirconia is an important area of research. Such studies can also be of broader relevance to advancing processing science of complex oxides.

We describe in detail the effect of ultra-violet irradiation on structural and interfacial phenomena at low temperatures (room temperature to 300°C) in zirconia thin films grown on semiconductor substrates. The effect of photon irradiation on nanoscale oxide film properties has gained significant interest in recent years. The interaction of light with oxygen influences the chemical activity of oxygen at the surface and results in changes in oxidation rate [10][11] oxygen stoichiometry [12] and kinetic phenomena.[13] This approach has been used to treat sol-gel derived oxide films for improving crystallinity and orientation, [14][15][16][17] and recently applied to films grown by physical vapour deposition.[18] Further, we have recently found that post deposition UV irradiation can introduce significant crystallinity change and densification in yttria doped

zirconia films even at room temperature.[19] This is likely due to incorporation of activated oxygen species produced by UV irradiation arising from proximity of the photon energy to the bond energy of oxygen molecule. [20] This low temperature photo-activation is unique since it offers selective enhancement of anion related kinetics. Another potential advantage of UV-enhanced processing is the ability to reduce annealing temperatures due to improved crystallinity thereby making it environmentally favourable and cost effective as well as minimizing un-desirable reactions.

In order to better understand photon-assisted phase stability and interfacial layer formation, it is beneficial to investigate the role of temperature and extrinsic defects introduced by aliovalent doping. Zirconia is a model system to investigate oxygen defect manipulation under photon irradiation because oxygen vacancies in the film can be controlled extrinsically by doping. Also it is a good ionic conductor even at low temperature, for example, Wakiya *et al.*, reported that oxygen diffusion can be induced in zirconia by electric-field at room temperature.[21] The present work discusses our systematic study of the effect of photon irradiation on structural and interfacial effects in zirconia thin films. Our results indicates photon induced process at low temperature is very sensitive to both aliovalent dopant concentration and annealing temperature. It suggests UV irradiation post-growth is an elegant route to tailor structure, morphology as well as defect concentration in oxide thin films.

2. Experimental

Pure zirconia and 9.5 % yttria doped zirconia (YDZ) pellets were evaporated by electron beam (e-beam) in a high vacuum chamber at room temperature to grow thin films on Ge (100) and Si (100) substrates at an estimated deposition rate of 0.2 Å/s. Substrates were cleaned by acetone and ethanol for 5 minutes respectively, then treated with buffered HF (2 %) for 2 minutes followed by de-ionized water cleaning before loading into the chamber. After deposition the samples were exposed to UV irradiation from a Hg vapor lamp under various conditions. The distance between UV lamp and sample was kept less than 5 cm during the

exposure. The substrate temperature during the photon irradiation was either room temperature or 300 °C. The process ambient is air, unless otherwise noted. The temperature increase due to irradiation was less than 5 °C even after the sample was exposed to UV for more than 17 hours and was monitored continuously. X-ray low angle reflectivity (XRR) and transmission electron microscopy (TEM) were used to evaluate film crystallinity, interface roughness and thickness. TEM samples were first dimpled and then thinned to electron transparency by Ar⁺ ion beam milling. JEOL 2100 and JEOL 2010F transmission electron microscopes were used in this study.

3. Results and Discussion

3.1 Role of aliovalent dopants on photon-induced structural changes (room temperature)

Figure 1(a) shows the XRR spectrum of e-beam grown ~130 Å thick film of pure zirconia grown on Ge substrate. The spectra were taken on as-deposited films, after 1h UV irradiation and after 4h UV irradiation in air. It is clear from the peak position of each fringe in the XRR spectrum that the thickness of ZrO₂ did not change even after 4 h UV irradiation in air. On the other hand, there is a difference in the amplitude of fringes between as-deposited and UV irradiated sample, especially in the high angle region. It is known that the decay of amplitude in high angle region of XRR spectrum depends on the roughness of interfaces.[22] The amplitude is large if the sample has smooth interfaces, while it is small if the sample has rough interfaces. Non-specular scattering hinders the interference of surface and interface reflected beam that is the origin of fringes. The absolute values of roughness were extracted from fitting the spectrum. The best fitting result indicates that the surface roughness had improved from ~ 11 Å to ~ 8 Å after 4h of UV irradiation. UV radiation produces ozone and radical oxygen, due to the closeness of photon energy to the O₂ and O₃ binding energy.[20] The existence of those activated oxygen species removes the barrier for chemisorption, therefore oxygen can be incorporated into the material even at room temperature.[23] These activated atomic oxygen may fill the vacancies available at the film surface to minimize the roughness.

Figure 1 (b) shows the XRR spectra of ~ 100 Å YDZ film grown on Ge. Interestingly, the effect of UV irradiation was more significant in yttria doped zirconia films than in undoped ZrO_2 films. The significant improvement in roughness is evident from the improvement of damped intensity oscillation at high angles. We found that the surface roughness reduced from ~ 13 Å to ~ 8 Å. Yttria (Y_2O_3) doping creates oxygen vacancies in zirconia (ZrO_2) through defect chemical reaction, $\text{Y}_2\text{O}_3 = 2\text{Y}'_{\text{Zr}} + \text{V}_\text{o}^{\bullet\bullet} + 3\text{O}_\text{o}^x$, therefore 9.5 mol % yttria doped zirconia used in this study is expected to contain ~ 4.75 mol % of oxygen vacancies with respect to the total number of available oxygen sites in un-doped zirconia. The large number of oxygen vacancies indicate several sites for oxygen incorporation, thus the effect of oxygen incorporation due to UV irradiation becomes significant in YDZ films than in un-doped zirconia films. The thickness of the YDZ film grown on Ge did not change upon room temperature UV irradiation. Figure 2 (a) shows the XRR spectra of ~ 120 Å ZrO_2 film grown on Si. Unlike the ZrO_2 film on Ge, the periodicity of the intensity oscillations changed slightly, suggesting that the top film thickness decreased upon UV irradiation. The initial thickness of 123 Å was reduced to 117 Å after the sample was exposed to UV for an hour. No thickness change was observed between UV irradiation of 1 h and 4 h, indicating the kinetics responsible for this change was self-limiting. Figure 2 (b) shows the XRR spectra changes taken from ~ 120 Å YDZ film grown on Si upon UV exposure for 2 hours at room temperature. As shown, the initial thicknesses of 118 Å reduced to 94 Å after UV exposure for 2 h in air. No further thickness change was observed even after UV irradiation for 4 hours. Thickness reduction in YDZ films was ~ 30 Å, while only 6 Å reduction was observed in un-doped ZrO_2 film.

The origin of this thickness reduction is likely the combination of interfacial layer formation and densification of YDZ layer. Figure 3 (a) and (b) shows the TEM cross-sectional micrograph of as-grown YDZ ~ 120 Å and ~ 330 Å on Si. By simply irradiating with UV for two hours at room temperature, crystallinity had improved and interfacial layer thickness increased from ~ 10 -15 Å to ~ 25 -30 Å as shown in Figure 4 (a) and (b). The inset fast Fourier transform (FFT) pattern shows changes in crystallinity upon UV irradiation and

was confirmed by x-ray diffraction.[19] This significant interfacial layer growth and structural changes are likely from the combination of various factors including the presence of activated oxygen species, potential gradient inside the film, and Zr-O bond cleavage under UV irradiation. A detailed analysis of the origin of this top layer thickness reduction can be found elsewhere.[19] It is important to note that interfacial layer growth is self-limited and weakly dependent on top YDZ film thickness, indicating diffusion in silicon dioxide is the rate-limiting step for interfacial layer growth. Those results indicate that ultra-thin interfacial growth ($\sim 10\text{-}20$ Å) under photon irradiation can introduce significant structural change in YDZ films even when the film is more than ten times thicker than the interfacial layer.

Interestingly, this significant difference in crystallinity was not observed in un-doped ZrO_2 films. Figure 5 (a) and (b) shows cross-sectional TEM micrograph of undoped $\text{ZrO}_2 \sim 135$ Å film and YDZ ~ 330 Å thick film grown on Si after 2 hours UV irradiation respectively. Interfacial layer thickness in undoped ZrO_2 increased from ~ 15 Å to ~ 20 Å, which is smaller compared to the YDZ case. This small difference in interfacial layer thickness increase and resultant top layer thickness decrease in undoped zirconia upon UV irradiation is in good agreement with XRR spectrum data shown in Figure 2 (a) and (b). No structural change was observed in ZrO_2 thin films grown on Si. This is confirmed by TEM micrographs and corresponding FFT pattern shown in Fig 5 (a), while YDZ treated in a same manner shows significant crystallization change as shown in Fig 5 (b). This difference between YDZ and undoped zirconia is also clearly seen in grazing incident x-ray diffraction scan shown in Figure 5 (c). Significant crystallinity change was clear from the appearance of cubic zirconia (111) peak from YDZ ~ 330 Å film after 2 hours UV, while no peak was detected in undoped $\text{ZrO}_2 \sim 430$ Å film after 2 hours UV irradiation.

3.2 Effect of temperature on photon induced phenomena (at 300 °C)

While almost no difference due to room temperature UV irradiation was found in undoped zirconia thin films grown on Ge, interesting differences were found when the films were annealed at 300 °C. Figure 6 shows x-ray diffraction pattern taken from two 1200 Å thick films grown identically. No peaks are present after annealing at 200 °C for 5 hours, and then significant crystallinity change took place in films at 300 °C (both with and without UV irradiation). This result indicates that photon irradiation has minimal effect on structural changes in thick undoped ZrO₂ films grown on Ge. However, the lattice parameter was found to be slightly different in the two cases. This is clearly seen in Fig 6 where the film annealed under UV shows peaks at $2\theta = 30.26^\circ$ ($d_{111} = 2.95$ Å) and 35.20° ($d_{200} = 2.55$ Å), corresponding to lattice constant ~ 5.10 Å, while the film annealed without UV shows $2\theta = 30.50^\circ$ ($d_{111} = 2.92$ Å) and 35.40° ($d_{200} = 2.53$ Å), corresponding to lattice constant ~ 5.07 Å.

In cubic fluorite structure, lattice parameter (d) can be calculated from ionic packing model

$$d = \frac{4}{\sqrt{3}} \{r(+) + r(-)\}$$

where $r(+)$ and $r(-)$ denotes the average ionic radii of cations and anions, respectively.[25] Glushkova *et al.* noted that aliovalently introduced oxygen vacancies have an effect on anion ionic radius, therefore lattice constant in doped fluorite structure cannot solely be explained by incorporation of cations that has a different ionic radius from that of host cation ions. They empirically obtained the radius of oxygen ion to be $r(-) = r(^{IV}O^{2-})(1 - X/4)^{1/3.6}$, where $r(^{IV}O^{2-})$ denotes the radius of an oxygen ion with a coordination number of 4 and X denotes the dopant content.[26] This relation indicates that oxygen deficiency decreases the lattice constant of fluorite-structured oxides. It is likely that the enhanced oxygen incorporation in UV-treated zirconia leads to an increase in lattice constant compared to the non-UV treated films. The

results are in agreement with previous reports on improved stoichiometry in zirconia films exposed to UV photons. [27]

Figure 7 shows cross-sectional TEM micrograph of YDZ ~ 130 Å /Ge structure after annealing at 300 °C for 2 hours (a) without UV and (b) with UV irradiation. No significant difference due to UV irradiation was observed in YDZ grown on Ge annealed at 300 °C, as seen from a comparison of TEM micrographs and corresponding FFT images. An interfacial layer (~ 20 Å thickness) was grown between YDZ/Ge with UV, while no interfacial layer is seen if the sample is annealed without UV. Also it is important to note that YDZ layer thickness did not change unlike the observations in YDZ/Si structure at room temperature. This interfacial layer growth is clearly seen in XRR plot as shown in Figure 7 (c). The peak position of the fringes indicates that UV assist process increases the thickness of top layer from ~ 135 Å to ~ 158 Å in 2 hours indicating the formation of a germanium oxide interfacial layer. This indicates germanium oxide can be formed by the combination of chemisorption energy assist by UV and thermal assist on diffusion of reactive species. Prior reports suggest that germanium oxide is thermodynamically stable below 400 °C and ~ 20 Å of germanium oxide formation is possible at 300 °C and in agreement with our observations.[28][29]

In contrast, the effect of UV becomes minimal in films grown on Si at 300 °C. Figure 8 (a) and (b) shows cross-sectional TEM of YDZ ~ 120 Å /Si structure after annealing at 300 °C for 2 hours (a) without UV and (b) with UV. Interfacial layer thickness increased from ~ 10 Å to ~ 25 Å in both cases and top YDZ layer thickness was not significantly changed. XRR spectrum shown in Fig 8 (c) also leads to same conclusion where top layer thickness reduced slightly from ~ 118 Å to ~ 105 Å, which is nearly half of thickness reduction observed at room temperature. From comparing results at 300 °C and room temperature, the origin of crystallinity change at room temperature is likely the combination of interfacial layer growth and lower thermal activation. This is clear from the fact that the crystallinity change was not introduced upon UV irradiation at 300 °C in YDZ/Si structure, while interfacial layer thickness increased to ~ 25 Å at both room

temperature and 300°C. The nearly identical FFT shown as inset in Fig 8 a and b shows that there is no significant change in crystallinity. Taking oxygen diffusivity in yttria 10 mol% doped zirconia to be $D_o = 3.4 \times 10^{-3} \exp(-0.99 \text{ eV} / kT)$ as reported by Kilo *et al.* ,[30] we can approximately estimate diffusion length to be $\sim 2.2 \text{ } \mu\text{m}$ at 300 °C for 2 hours, while $\sim 0.2 \text{ nm}$ at 25 °C. This indicates that diffusion length of oxygen is enough to penetrate from top surface to the YDZ/Si interface at 300 °C. It is likely that the interfacial oxidation proceeds mostly by oxygen diffusing from the top surface at 300 °C. On the other hand, the diffusivity of oxygen is not enough to penetrate through the film at room temperature, while oxygen atoms in the ZrO_2 network may be consumed to form SiO_2 under photon irradiation due to Zr-O bond cleavage. The unchanged total thickness of the film (i.e., interfacial layer (IL) + YDZ layer) at room temperature after photon irradiation supports this hypothesis. The crystallinity change likely originates from a combination of limited oxygen diffusivity at low temperature, Zr-O bond cleavage upon UV irradiation, and consumption of Zr-O network oxygen for Si interfacial layer oxidation near YDZ/(SiO_2)/Si interface.

4. Summary and Conclusions

i) At room temperature, interfacial layer growth, film densification and changes in crystallinity were observed in YDZ films grown on Si, while there was minimal difference in films grown on Ge. Ultra-thin interfacial layer growth ($\sim 10\text{-}20 \text{ } \text{\AA}$) under photon irradiation is likely responsible for the significant structural change in YDZ films even when the film is more than 10 times thicker than the interfacial layer.

ii) Structural changes in zirconia thin films were introduced within an hour and no further change was observed even after 4 hours of UV irradiation, indicating UV photon induced phenomena is self-limited process.

iii) A comparison of un-doped and yttria doped zirconia films indicate yttria doping significantly assists structural changes in films under UV irradiation.

iv) YDZ top layer thickness does not introduce significant difference in photon introduced phenomena (interfacial layer growth and crystallinity change) at room temperature if the thickness is less than ~ 330 Å.

v) At 300 °C, crystallinity of zirconia films improved due to annealing regardless of substrate type, UV irradiation and doping concentration, however there was a slight difference in the lattice constant likely due to differences in oxygen concentration.

vi) An interfacial layer was grown between YDZ and Ge at 300 °C under UV, while sharp interface was found to be stable in the absence of UV irradiation.

Overall, our results show that UV irradiation offers an elegant route to manipulate oxygen defects at relatively low temperatures and can influence crystallinity, stoichiometry and interfacial phenomena in multi-component oxides. We anticipate these results to provide mechanistic understanding of photon irradiation-induced phenomena in thin film oxides and may open up routes to tailor properties.

References

- [1] A. H. Heuer and L. W. Hobbs (Editors), *Advances in Ceramics*, Vol. 3 (American Ceramic Society, Columbus, OH, 1981).
- [2] G. D. Wilk, R. M. Wallace and J. M. Anthony, *J. Appl. Phys.*, **89**(10), 5243 (2001).
- [3] S. Ramanathan, P. C. McIntyre, S. Guha and E. Gusev, *Applied Physics Letters*, **84** (3), 389 (2004).
- [4] H. Huang, M. Nakamura, P. C. Su, R. Fasching, Y. Saito and F. B. Prinz, *Journal of the Electrochemical Society*, **154** (1): B20 (2007).
- [5] J. Fleig, H. L. Tuller and J. Maier, *Solid State Ionics*, **174**, 261 (2004).
- [6] H. G. Scott, *Journal of Materials Science*, **10**, 1527 (1975).
- [7] E. C. Subbarao and H. S. Matt, *Solid State Ionics*, **11**, 317 (1984).
- [8] N. Wakiya, M. Yoshida, T. Kiguchi, K. Shinozaki and N. Mizutani, *Thin Solid Films*, **411**, 268 (2002).
- [9] M. Tsuchiya, A. M. Minor and S. Ramanathan, *Philosophical Magazine*, **87** (36), 5673 (2007).
- [10] C. L. Chang and S. Ramanathan, *Journal of Electrochemical Society*, **154** (7), G160 (2007).
- [11] S. Ramanathan, G. D. Wilk, D. A. Muller, C. M. Park and P. C. McIntyre, *Applied Physics Letters*, **79** (6), 2621 (2001).
- [12] S. Ramanathan, D. A. Muller, G. D. Wilk, C. M. Park and P. C. McIntyre, *Appl. Phys. Lett.*, **79** (20), 3311 (2001).
- [13] M. Tsuchiya and S. Ramanathan, *Appl. Phys. Lett.*, **92**, 033107 (2008).
- [14] N. Asakuma, H. Hirashima, H. Imai, T. Fukui, A. Maruta, M. Toki and K. Awazu, *Journal of Applied Physics*, **92** (10), 5707 (2002).
- [15] H. Imai, A. Tominaga, H. Hirashima, M. Toki and N. Asakuma, *Journal of Applied Physics*, **85** (1), 203 (1999).
- [16] K. Nishizawa, T. Miki, K. Suzuki and K. Kato, *Journal of Materials Research*, **18** (4), 899 (2003).

- [17] K. Nishizawa, T. Miki, K. Suzuki and K. Kato, Journal of Materials Research, **20** (11), 3133 (2005).
- [18] Y. Zhao, K. Kita, K. Kyuno and A. Toriumi, Japanese Journal of Applied Physics, **46** (7), 4189 (2007).
- [19] M. Tsuchiya and S. Ramanathan, Appl. Phys. Lett., **91**, 253104 (2007).
- [20] A. Kazor and I. W. Boyd, Journal of Applied Physics, **75** (1), 227 (1994).
- [21] N. Wakiya, N. Tajiri, T. Kiguchi, N. Mizutani, J. S. Cross and K. Shinozaki, Japanese Journal of Applied Physics, **45** (11), 8827 (2006).
- [22] M. Birkholz, "*Thin film analysis by x-ray scattering*", Wiley-VCH, Weinheim, Germany (2006).
- [23] S. Ramanathan, D. Chi, P. C. McIntyre, C. J. Wetteland and J. R. Tesmer, J. Electrochem. Soc. **150** (5), F110 (2003).
- [24] A. Karthikeyan and S. Ramanathan, Applied Physics Letters, **90**, 093107 (2007)
- [25] M. W. Barsoum, "*Foundamenrals of Ceramics*", McGraw-Hill, New York (1997).
- [26] V. B. Glushkova and M. V. Kravchinskaya, Ceramics International, **11** (2), 56 (1965).
- [27] S. Ramanathan, P.C. McIntyre, J. Luning, P. Pianetta and D.A. Muller, Philosophical Magazine Letters, **82**, 519 (2002).
- [28] Y. Kamata, Materials Today, **11** (1-2), 30 (2008).
- [29] Y. Kamata, Y. Kamimuta, T. Ino and A. Nishiyama, Japanese Journal of Applied Physics, **44** (4B), 2323 (2005).
- [30] M. Kilo, C. Argirusis, G. Borchardt, and R. A. Jackson, Phys. Chem. Chem. Phys., **5**, 2219 (2003).
- [31] S. C. Singhal and K. Kendall, "*High Temperature Solid Oxide Fuel Cells*", Elsevier, Oxford, (2003) pp 84
- [32] S. Raz, N. Stelzer, R. Kalish, J. Maier and I. Riess, Solid State Ionics, **175**, 323 (2004).
- [33] N. Wakiya, N. Tajiri, T. Kiguchi, N. Mizutani, J. S. Ctross and K. Shinozaki, Japanese Journal of Applied Physics, **45** (20), L525 (2006)

Figure 1: X-ray reflectivity spectra taken from (a) e-beam grown $\text{ZrO}_2 \sim 120 \text{ \AA}$ film grown on Ge before and after UV irradiation for 1 h and 4 h at room temperature and (b) e-beam grown YDZ $\sim 100 \text{ \AA}$ film grown on Ge before and after UV irradiation for 2 h at room temperature.

Figure 2: X-ray reflectivity spectra taken from (a) e-beam grown $\text{ZrO}_2 \sim 120 \text{ \AA}$ film grown on Si before and after UV irradiation for 1 h and 4 h at room temperature and (b) e-beam grown YDZ $\sim 120 \text{ \AA}$ film grown on Si before and after UV irradiation for 2 h and 4 h at room temperature.

Figure 3: Cross-sectional TEM micrograph of as-grown YDZ (a) $\sim 120 \text{ \AA}$ and (b) $\sim 330 \text{ \AA}$ thickness films.

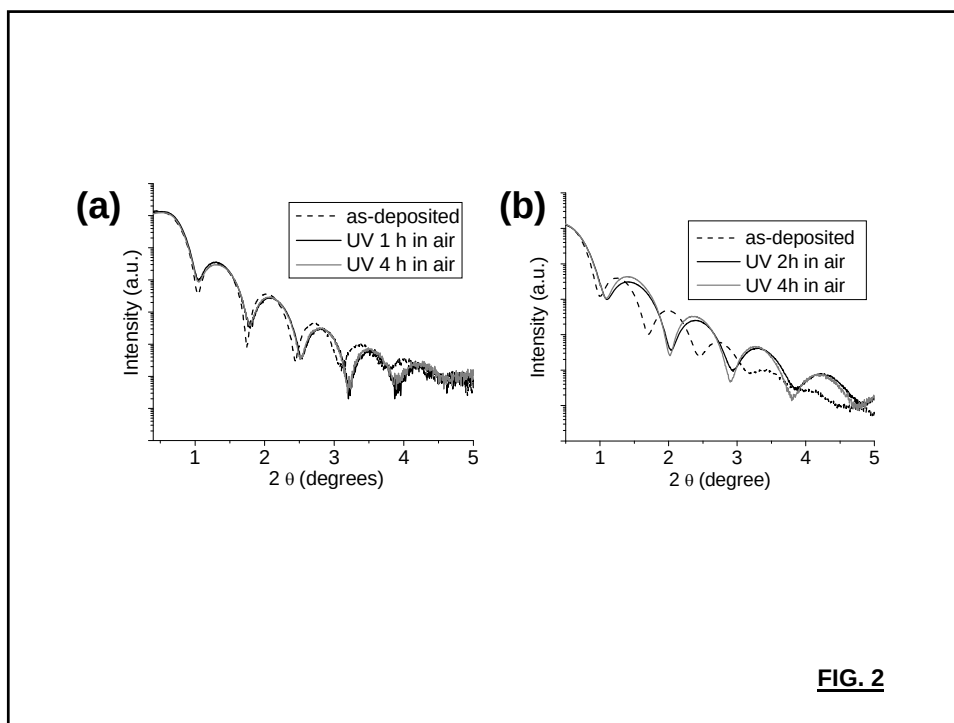
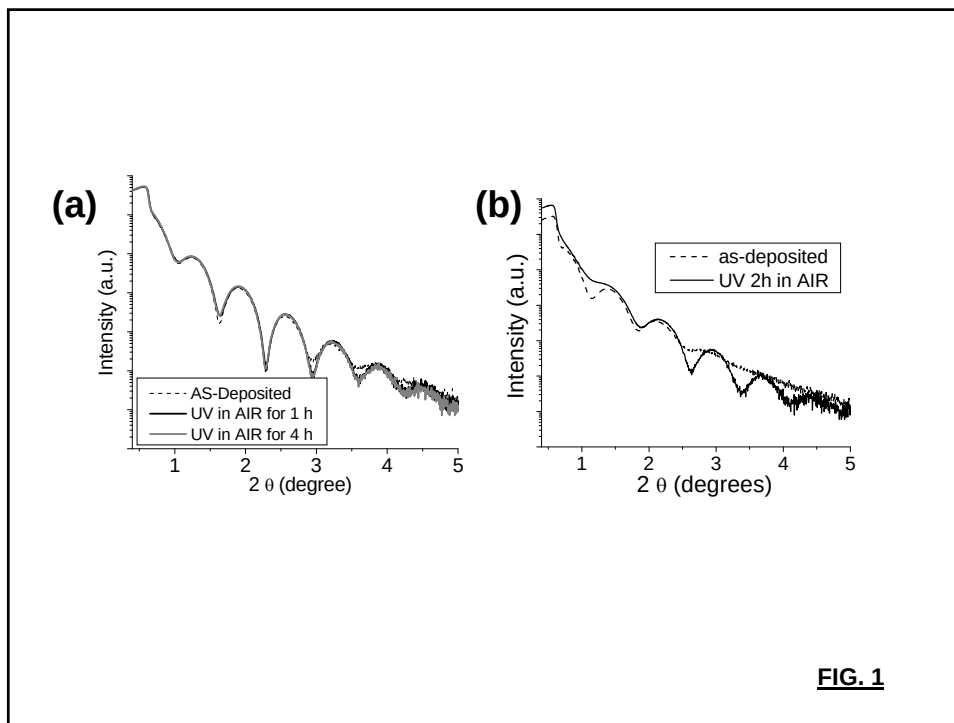
Figure 4: Cross-sectional TEM micrograph of YDZ (a) $\sim 120 \text{ \AA}$ and (b) $\sim 330 \text{ \AA}$ thick films after UV irradiation for 4 hours.

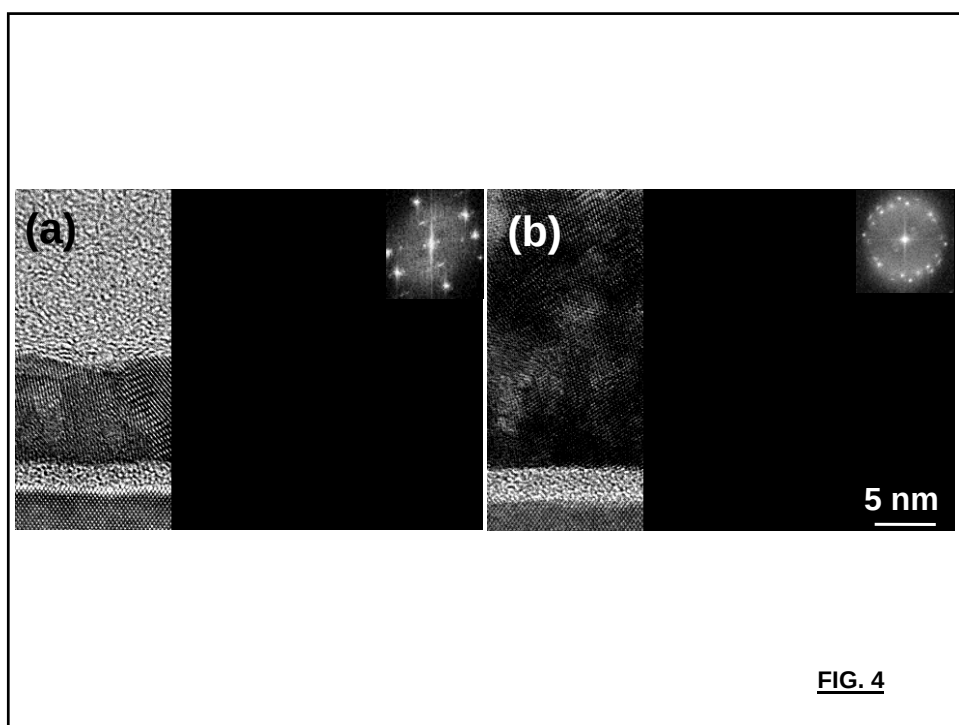
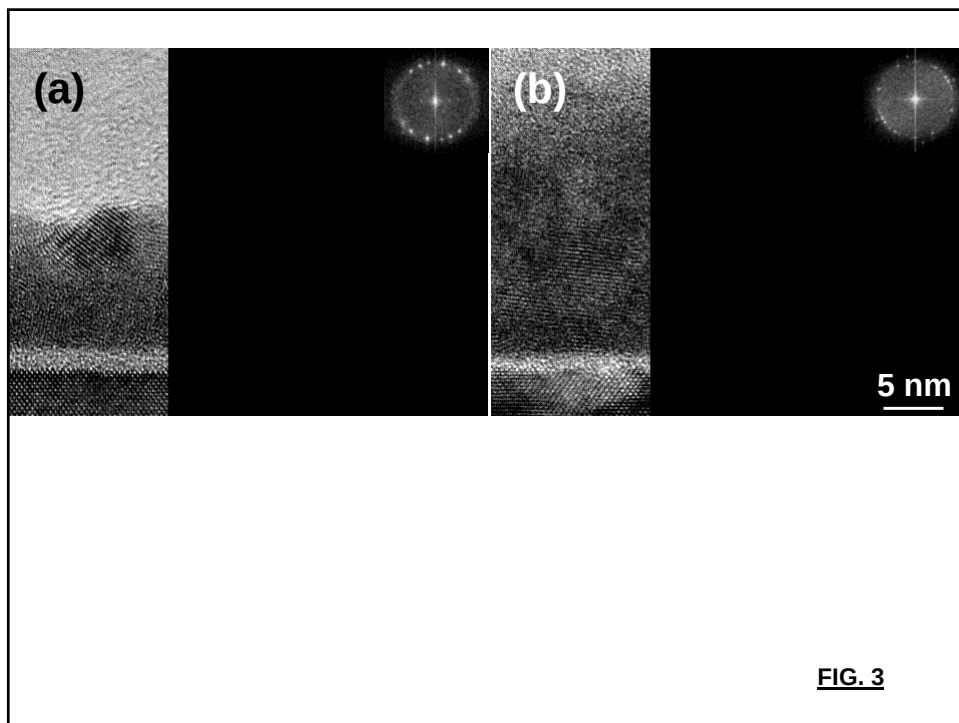
Figure 5: (a) Cross-sectional TEM micrograph of undoped $\text{ZrO}_2 \sim 130 \text{ \AA}$ after UV irradiation for 2 h at room temperature (b) cross-sectional TEM micrograph of $\sim 330 \text{ \AA}$ YDZ films after 2 h at room temperature (c) Grazing incidence x-ray diffraction scan of $\sim 430 \text{ \AA}$ ZrO_2 and $\sim 330 \text{ \AA}$ YDZ films.

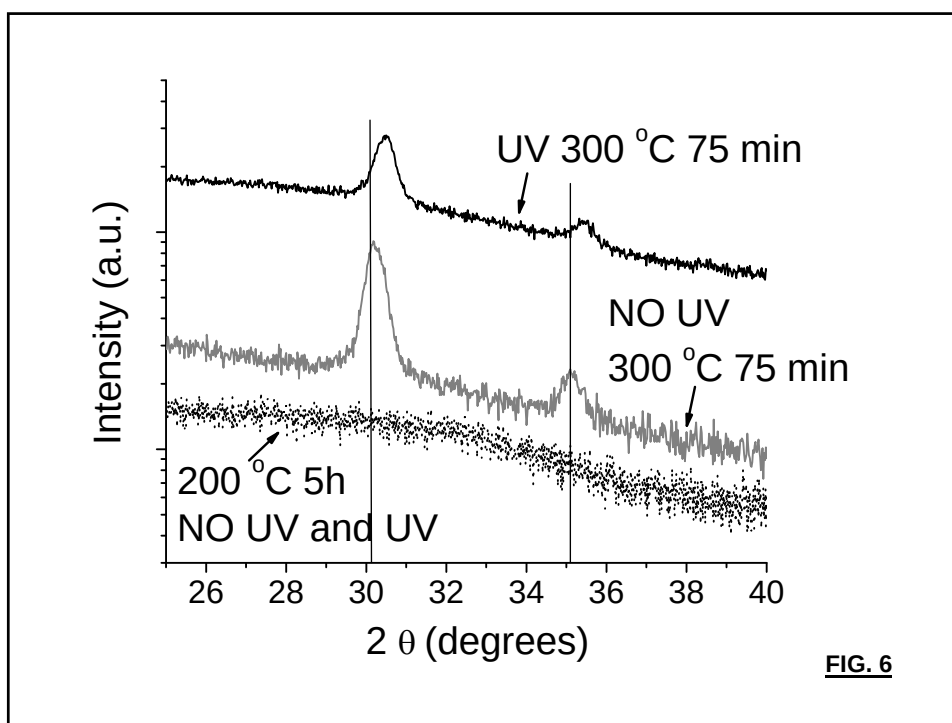
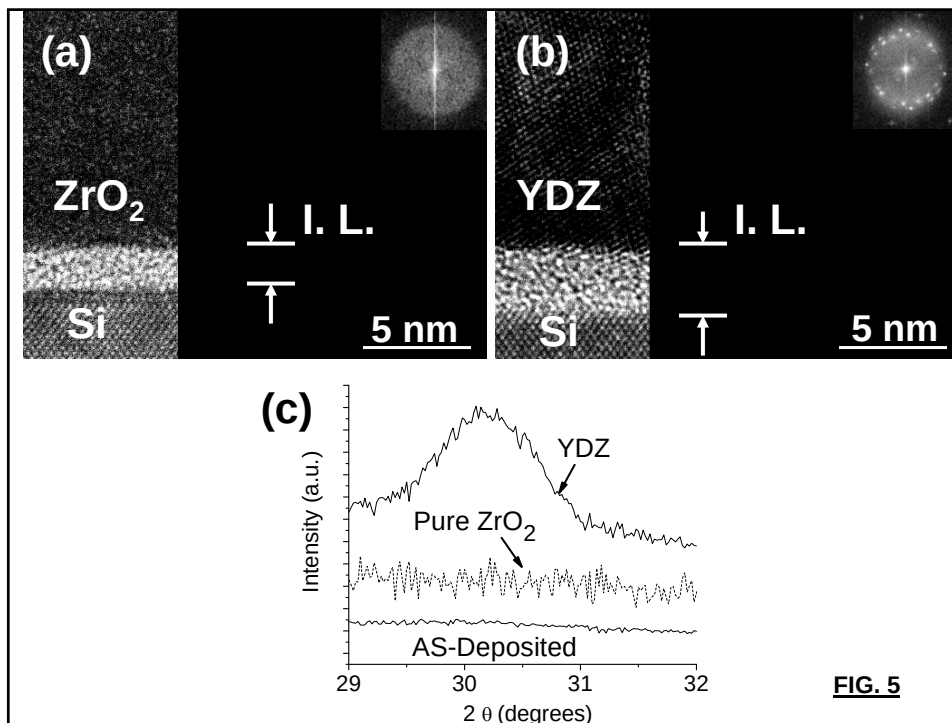
Figure 6: Grazing incidence x-ray diffraction of $\text{ZrO}_2 \sim 1200 \text{ \AA}$ thick films annealed under UV and no UV irradiation.

Figure 7: TEM cross-section micrograph of YDZ $\sim 135 \text{ \AA}$ films grown on Ge. (a) annealed without UV at 300°C for 2 hours and (b) annealed with UV at 300°C for 2 hours. (c) X-ray reflectivity data of $\text{ZrO}_2 \sim 135 \text{ \AA}$ films annealed with and without UV exposure at 300°C for 2 hours.

Figure 8: TEM cross-section micrograph of YDZ ~ 120 Å films grown on Si. (a) annealed without UV at 300 °C for 2 hours and (b) annealed with UV at 300 °C for 2 hours. Corresponding x-ray reflectivity data is shown in (c).







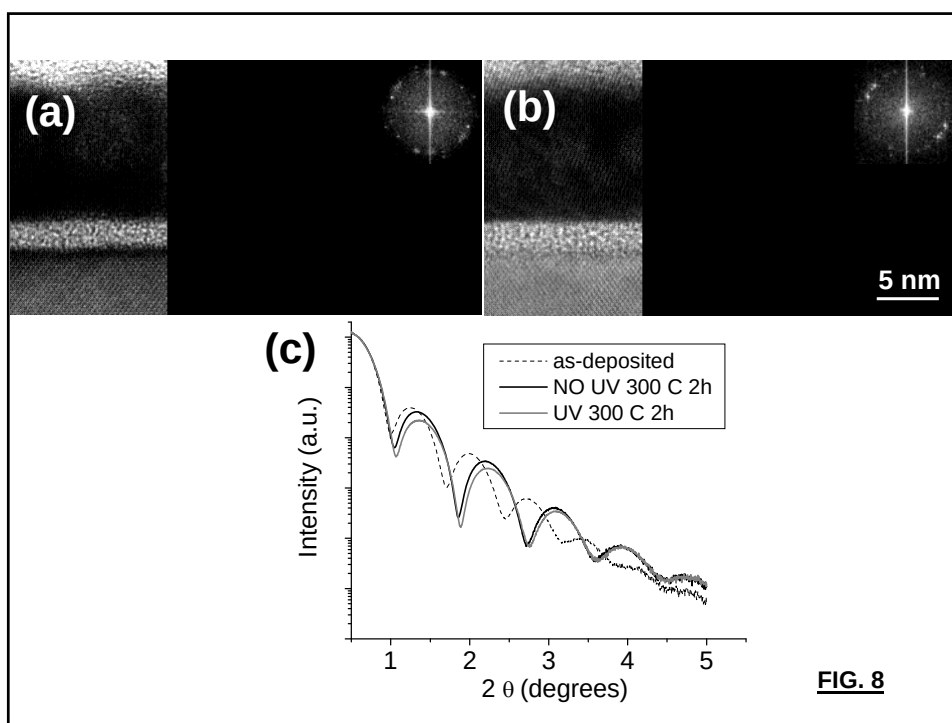
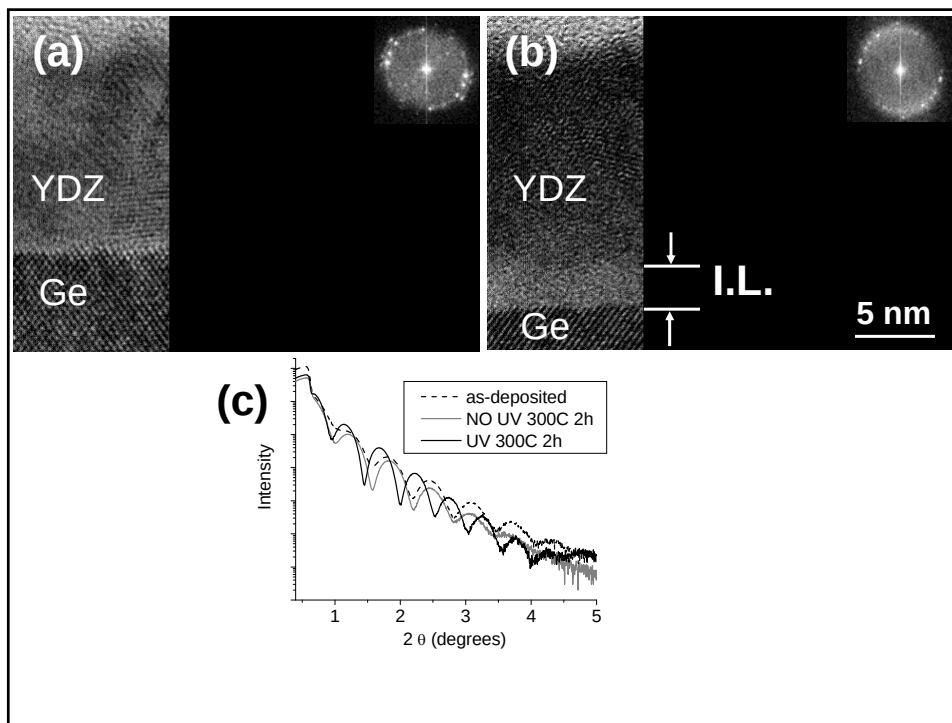


FIG. 8