Piezoelectric Response in WO3-x Thin Films by Aluminum Clustering

Pamela Pineda-Domínguez  
Universidad Autónoma de Ciudad Juárez

Manuel Ramos  
manuel.ramos@uacj.mx  
Universidad Autónoma de Ciudad Juárez

John Nogan  
Center for Integrated Nanotechnologies

Oscar Alberto López-Galán  
Universidad Autónoma de Ciudad Juárez

José Luis Enríquez-Carrejo  
Universidad Autónoma de Ciudad Juárez

Torben Boll  
Karlsruhe Institute of Technology

Abel Hurtado-Macías  
Centro de Investigación en Materiales Avanzados

Jorge López-Gallardo  
The University of Texas at El Paso

Yahir Garay  
The University of Texas at El Paso

Héctor Camacho-Montes  
Universidad Autónoma de Ciudad Juárez

Martin Heilmiaier  
Karlsruhe Institute of Technology

Research Article

Keywords: tungsten trioxide, aluminum, piezoelectric, atom probe tomography, materials.

DOI: https://doi.org/10.21203/rs.3.rs-384370/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. 
Read Full License
Abstract

We report piezoelectric response of $d_{33} = 35 \pm 5 \text{ pm V}^{-1}$ on aluminum doped tungsten trioxide thin films (Al-WO$_3$ - $\lambda$), prepared by RF-sputtering and post annealing treatment in air atmosphere. Using XPS characterization indicate a stoichiometry of WO$_{2.7}$ and Raman a distorted octahedral tungsten vibration mode of monoclinic WO$_3$ at 236.9 cm$^{-1}$, 691 cm$^{-1}$ and 803 cm$^{-1}$ corresponding to O-W-O chemical bonds. The grazing incidence X-ray diffraction revealed a non-centrosymmetric monoclinic (P2$_1$/c) and tetragonal (P4/nmm) mixed phases of WO$_{3-x}$ with islands of piezoelectric domains as observed by atomic force microscope, additionally atom probe tomography revealed diffusion of aluminum ions from Al$_2$O$_3$ substrate.

1.0 Introduction

Outstanding applications in the field of Internet of Things (IoT) [1]–[3] and micro-electromechanical systems (MEMS) [4, 5] have increased the demand for environmentally friendly, low cost, and reliable materials to fabricate several types of sensors, actuators and power components [6–9]. This has expanded the interest on properties such as electrochromism and piezoelectricity in various materials [10–12]. Piezoelectric materials have gained importance in modern day technology due their wide range of applications, from positioners in electronic microscopes, crystal oscillators, sound and vibration sensors, and energy harvesting devices [13–19]. Piezoelectricity occurs mainly in non-centrosymmetric structures [20]–[23], which refers to those lacking an inversion point, i.e., a point or atom position at specific coordinates inside the Bravais unit cell, with respect to a crystallographic plane; in the spatial distribution this causes uneven distribution of electronic states and when a mechanical force is applied part of those accumulated electron charges are released, causing a piezoelectric response, as described extensively in the literature [21], [24]–[28]. Several materials can exhibit piezoelectricity to some degree, this includes ceramic materials [20], [29], polymers [23, 24] and semiconductors [31], with lead zirconate titanate, also known as PZT, is one of most common piezoelectric ceramics as reported in the literature, with remarkable piezoelectric response derived from interaction at morphotropic phase boundary (MPB) [25]. Sustainable environmental concerns and also that it is an insulator [27, 28] has caused an intensified on-going research worldwide in search for lead-free conducting piezoelectric materials [27, 29, 30], and previous investigations in the materials field indicate that piezoelectric semiconductors are potential candidates due to intrinsic piezoelectricity and conductivity [36]. Also, some binary compounds such as ZnO and AlN, have been considered attractive piezoelectric materials and currently are under extensive research [25, 32], some reports indicates addition of ZnO or WO$_3$ as dopants in PZT or in BaTiO$_3$–SrTiO$_3$ ceramics can induce piezo-response [33–36]. Recently, Chen et al. successfully used ZnO-WO$_{3-x}$ nanorods for piezoelectric-photoelectrochemical water splitting due to intrinsic ZnO piezoelectricity and the fact that WO$_{3-x}$ charge carrier concentration can be tuned in function of oxygen vacancies [42]. Corby et al. found that vacancy concentration of 2% for stoichiometric oxides meaning oxygen concentration, can maximize photocurrent in water splitting performance [43], similar to the
results reported by Soltani et al. [44]. Kim et al. reported piezoelectric response in an oxygen-deficient WO$_{2.96}$ film with a $d_{33}$ coefficient of 7.9 pm/V, attributed to the non-centrosymmetric structures within film thickness, that corresponds to monoclinic and tetragonal phases [45]. In this communication, we are reporting piezoelectric response for aluminum doped WO$_3$ thin films annealed at 400°C, along with extensive characterization by grazing incidence X-ray diffraction (GIXRD) and atom probe tomography (APT).

2.0 Results And Discussion

Piezoelectric response by PFM

WO$_3$ thin films were deposited on sapphire with a resulting thickness of 225 nm and subsequently annealed at various temperatures, see experimental methods section. A piezoelectric response was found in the film annealed at 400°C, determined by characterization using piezo force microscopy technique in dual AC resonance tracking (DART) mode, as described extensively in [22, 26–28, 46, 47]. The surface topography of this film is shown in Fig. 1a, and Fig. 1b) and 1c) corresponds to the piezo force microscopy signal phase before and after measurements, revealing a local hysteresis loops; hysteresis loops corresponding to red circles, where piezo response domains appear as yellow, white and violet colored regions show polarization direction piezoelectric domains, as described by Kholkin et al. [27]. The white regions are positive domains, i.e., polarization pointing towards the bottom electrode, which occurred by switching domains as observed in hysteresis loops shown in Fig. 1e. Furthermore, ferroelectric behavior was observed in the sample annealed at 400°C from hysteresis loops in phase and piezoelectric coefficient ($d_{33}$) versus AC applied bias voltage as shown in Fig. 1f. The piezoelectric coefficient was determined by positioning the cantilever across a large grain of Al-WO$_{3-x}$ (red circle). The amplitude (nm) versus AC bias voltage (V) exhibited a butterfly loop as presented in Fig. 1d and it is related to piezoelectric deformation under an applied AC bias voltage demonstrating a local polarization switching behavior [28]. The latter indicates that a phase difference of 180° polarization switching under DC bias voltage related to the existence of piezoelectric domains and local $d_{33}$ coefficient can be estimated by $(V-V_1)d_{33} = D-D_1$, where $D$ is the measured piezoelectric deformation or amplitude, $V$ is applied voltage, $D_1$ is the piezoelectric deformation, and $V_1$ is the applied voltage at the intersection as described by Roelofs et al. [28]. The coercive voltage (2.7 V) was evaluated using the equation $(V_c^+ - V_c^-)/2$ where $V_c^+$ and $V_c^-$ are the forward and reverse coercive bias voltages, respectively. The piezoelectric coefficient ($d_{33}$) of 35 ± 5 pmV$^{-1}$ was measured at the maximum voltage of 10 V for the film annealed at 400°C, which is four times higher than that reported by Kim et al. [45] for WO$_{2.9}$ and the highest value found in the literature for this material, indicating a potential use in piezoelectric devices [48].

The measured $d_{33}$ coefficient is assume to occur due to non-centrosymmetric phases in combination with potential oxygen vacancies and aluminum doping induced a different stoichiometric composition of WO$_3$$_{3-x}$ films, mainly for those processed at 400°C in agreement with reports as found in the literature [38, 48–
And confirmed by XPS measurements (Supplemental material) which reveals a stoichiometry of WO$_{2.7}$ in the surface of the film annealed at 400°C and in agreement with grazing incidence x-ray diffraction (GIXRD) and atom probe tomography (APT) as presented in this communication.

Crystallographic structure as determined by GIXRD

As presented in Fig. 2, an evolution of crystallinity occurred on the films from room temperature to annealing process at 400°C and 550 ºC corresponding to polycrystalline amorphous structure, reflections at 23.1° corresponds to (001), (021) and (121) and corresponds to monoclinic WO$_3$-$x$ phase (γ-WO$_3$-$x$) [57], [59]–[61] with space group P2$_1$/c, a tetragonal WO$_3$-$x$ phase (α-WO$_3$-$x$) with P4/nmm space group is formed for sample at 400°C in agreement with literature [61, 62]. The Raman spectra indicate a distorted octahedral tungsten vibration mode of monoclinic WO$_3$-$x$ at 236.9 cm$^{-1}$, 691 cm$^{-1}$ and 803 cm$^{-1}$ attributed to bending O-W-O bonds and symmetric/antisymmetric stretching of W-O bonds (see supplemental material). However, as the annealing temperature increased and evolution of phases occurred with γ-WO$_3$-$x$ or α-WO$_3$-$x$ for 500°C and 550°C, respectively as observed. Furthermore, diffractions at ~37º which corresponds to (111) planes of metallic aluminum (FCC), only appear at 400°C and not at 500°C and 550°C, our believe is that aluminum clusters is formed by interdiffusion from sapphire substrates (Al$_2$O$_3$) during annealing process, in agreement with Li et al. oxygen vacancies can promote defects and dislocation; and potentially can induce diffusion of aluminum ions on lattice sites within WO$_3$ [64]; because critical temperature of aluminum diffusion is reached at above 300°C in agreement with previous reports, and revealed by atom probe tomography, Fig. 3. Thus, segregated aluminum induces formation of mixed α-WO$_3$-$x$ and γ-WO$_3$-$x$ phases in agreement with previous reports [52], [65]; as it is described usually heavy metallic ions like induces recrystallization in thin films [66]. Also, metallic species such as gold (Au) induces phase change from triclinic to monoclinic in WO$_3$ [67]. In here, we were able to determine that aluminum is diffused creating changes on the electronic states mainly on island form over film and mixed monoclinic and tetragonal (α-WO$_3$-$x$ and γ-WO$_3$-$x$) specially when is processed at 400°C, in agreement with Ahart et al. [25] and Ibrahim et al. [68] who explained in detail that mixed phases can produce a morphotropic phase boundary (MPB).

Chemical distribution by atom probe tomography

In order to investigate chemical volume distribution a series of atom probe tomography characterizations were completed, which is an abrasive technique used to obtain time of flight mass spectrometry from events occurred due to laser pulse ionic evaporation at high-vacuum as described in the literature [69], for all APT measurements a well-defined interface between WO$_3$ film and Al$_2$O$_3$ substrate was revealed. From mass spectrum it was possible to achieve chemical composition distribution mainly at the WO$_3$ film thickness (0-400nm) and traces of aluminum, oxygen and tungsten was found as shown in Fig. 3. Tungsten concentration remains around 27% during annealing process and oxygen concentration is about 70% at 400 ºC with strong traces of aluminum (~3%) which forms clusters, as shown in Fig. 3a; it is our believe this clusters are formed during annealing process by ionic diffusion from sapphire
substrate due to voids occurred by oxygen vacancies which allowed aluminum ions to undergo onto WO$_3$
[56], [65], which is in agreement with mixed phases as encountered by grazing incidence x-ray diffraction.
For sample processed at 500°C lower concentration (>1%) of aluminum ions is found and corresponds
mainly to $\alpha$-WO$_{3-x}$ as shown in Fig. 3b and no traces of grain boundaries was found for all samples.

3.0 Conclusions

We report a piezoelectric response with $d_{33} = 35 \pm 5$ p/V for Al-WO$_{3-x}$ in thin films processed at 400°C.
The grazing incidence x-ray and atom probe indicates that piezo-response effect is caused by aluminum
diffusion creating mixed phase between $\gamma$-WO$_{3-x}$ (monoclinic) and $\alpha$-WO$_{3-x}$ (tetragonal) corresponding
to a non-centrosymmetric. And we found that at elevated annealing temperatures (>400°C) film
recrystallizes in $\alpha$-WO$_{3-x}$ followed by $\gamma$-WO$_{3-x}$ causing a reorder to piezoelectric domains, as confirmed
by atom probe tomography where no clustering of aluminum was encountered for sample processed at
500°C.

Experimental Methods

RF magnetron sputtering

The tungsten trioxide (WO$_3$) thin films were deposited by radio frequency magnetron sputtering technique
using a 99.99% pure WO$_3$ disk as target and Al$_2$O$_3$ as substrate. The base pressure was set up to $1 \times 10^{-6}$
Torr before allowing Ar into the chamber as plasma source. The deposition rate was 1 Å/s, at a working
pressure of 3 mTorr and 225 W of RF power. The wafer was cut into several samples for subsequent
annealing process at temperatures of 300 °C, 400 °C, 500 °C and 550 °C, for 45 min with a 15 min ramp
down, in air. A film thickness of ~220 nm was measured for the as-deposited film using profilometry.

Piezo Force Microscopy (PFM)

Domain imaging, switching and piezoelectric hysteresis loops were investigated by piezoresponse force
microscopy (PFM) using the Dual AC Resonance Tracking (DART) mode, in a commercial Atomic Force
Microscope (AFM) model Infinity 3D Asylum Research with two internal lock-ins amplifiers. The PFM was
operated in vertical mode with an AC voltage amplitude of 5 $V_{pk-pk}$ and at a drive frequency of 398 kHz
far below the resonance of the cantilever, applied between the bottom electrode and the Pt/Ir conductive
tip during imaging PFM. To achieve the measurement of local polarization (hysteresis loops) a voltage of
-10 to 10 $V_{pk-pk}$ was applied using the spectroscopy PFM mode.

Grazing Incidence X-Ray Diffraction (XRD)

Crystallographic structure was obtained with the aid of Panalytical Empyrean system, with CuK$_\alpha$ radiation
source ($\lambda=1.54$ Å) at an operating accelerating voltage of 40 kV and an emission current of 30 mA.
Scanning angle was varied from 20° to 80° with a step size of 0.05°.

**Atom Probe Tomography (APT)**

Three-dimensional chemical distribution for W, O and Al was obtained with a Cameca® LEAP 4000X high-resolution system, equipped with a UV laser ($\lambda \sim 355$ nm). All measurements were taken at a set temperature of 50 K with an evaporation rate of 0.2 and a laser frequency of 100 kHz. The laser beam was set to 20 pJ/V, and all data were reconstructed from SEM images using the Cameca IVAS® 3.6.14 package. Additional samples were prepared by directly coating the micro tip coupons provided by the CAMECA with the multilayer sputtering system. The samples were prepared by annular milling with the aid of the focused ion-beam (FIB) instrument models FEI® Strata or Zeiss Auriga, both equipped with dual beam. The surface was protected with an additional platinum layer deposited from a precursor gas within the SEM-FIBs to reduce amorphization of film matrix.

**Declarations**

**Authors Contribution**

P.M.P.D, M.R., J.N. and O.A.L.G. completed all sample preparation at Center for Integrated Nanotechnologies-Albuquerque, NM. J.L.E.C. and P.M.P.D. performed the Raman measurements. T.B. and M.H. performed atom probe tomography characterization at Karlsruhe Nano and Micro Facility. A. H.M. measure piezo-electric properties at Centro de Investigación en Materiales Avanzados-Chihuahua. J. L. and Y. G. performed XPS measurements at University of Texas at El Paso. Data analysis was completed by P.M.P.D., H.C. and O.A.L. G.; and manuscript was mainly typed by P.M. P.D., O. A. L.G., J.L.E.C., M.H. and M.R.

**Acknowledgments**

Authors thank: Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000 under external user proposal #2018AU0133. We are grateful to the Karlsruhe Micro and Nano Facility (KNMF) of Karlsruhe Institute of Technology for usage of Atom Probe Tomography and FIB instruments and to IAM-WK of Karlsruhe Institute of Technology. The Laboratorio Nacional de Nanotecnología de Centro de Investigación en Materiales Avanzados (CIMAV-Chihuahua) for the usage of electron microscopy and characterization equipment. P. Pineda-Domínguez and M. Ramos thank Dirección General de Vinculación e Intercambio of Universidad Autónoma de Ciudad Juárez for travel award support and Instituto de Ingeniería y Tecnología of UACJ. Pineda-Domínguez thank the graduate scholarship sponsor program of Consejo Nacional de Ciencia y Tecnología-México, scholarship number 956889.
References

1. Cánovas, R., Parrilla, M., Blondeau, P. & Andrade, F. J. A novel wireless paper-based potentiometric platform for monitoring glucose in blood. *Lab Chip.* 17, 142500–142507 https://doi.org/10.1039/C7LC00339K (2017).

2. Novell, M., Guinovart, T., Blondeau, P., Rius, F. X. & Andrade, F. J. A paper-based potentiometric cell for decentralized monitoring of Li levels in whole blood. *Lab Chip.* 14 (no. 7), 1308 https://doi.org/10.1039/c3lc51098k (2014).

3. Zanella, A., Bui, N., Castellani, A., Vangelista, L. & Zorzi, M. “Internet of Things for Smart Cities,” IEEE Internet Things J., vol. 1, no. 1, pp. 22–32, Feb 2014, doi: 10.1109/JIOT.2014.2306328.

4. Yuan, K. et al. “Fabrication of a Micro-Electromechanical System-Based Acetone Gas Sensor Using CeO$_2$ Nanodot-Decorated WO$_3$ Nanowires,” *ACS Appl. Mater. Interfaces*, vol. 12, no. 12, pp. 14095–14104, Mar. 2020, doi: 10.1021/acsami.9b18863.

5. Andreu-Perez, J., Leff, D. R., Ip, H. M. D. & Yang, G. Z. “From Wearable Sensors to Smart Implants—Toward Pervasive and Personalized Healthcare,” IEEE Trans. Biomed. Eng., vol. 62, no. 12, pp. 2750–2762, Dec 2015, doi: 10.1109/TBME.2015.2422751.

6. Kumar, A. Methods and Materials for Smart Manufacturing: Additive Manufacturing, Internet of Things, Flexible Sensors and Soft Robotics. *Manufacturing Letters.* 15, 122–125 https://doi.org/10.1016/j.mfglet.2017.12.014 (Jan. 2018).

7. Spearing, S. M. Materials issues in microelectromechanical systems (MEMS). *Acta Mater.* 48 (no. 1), 179–196 https://doi.org/10.1016/S1359-6454(99)00294-3 (Jan. 2000).

8. Zaia, E. W., Gordon, M. P., Yuan, P. & Urban, J. J. Progress and Perspective: Soft Thermoelectric Materials for Wearable and Internet-of-Things Applications. *Adv. Electron. Mater.* 5 (no. 11), 1800823 https://doi.org/10.1002/aelm.201800823 (Nov. 2019).

9. Haras, M. & Skotnicki, T. Thermoelectricity for IoT – A review. *Nano Energy.* 54, 461–476 https://doi.org/10.1016/j.nanoen.2018.10.013 (Dec. 2018).

10. Mortimer, R. J., Dyer, A. L. & Reynolds, J. R. Electrochromic organic and polymeric materials for display applications. *Displays.* 27 (no. 1), 2–18 https://doi.org/10.1016/j.displa.2005.03.003 (Jan. 2006).

11. Terrones, H., López-Urías, F. & Terrones, M. “Novel hetero-layered materials with tunable direct band gaps by sandwiching different metal disulfides and diselenides,” Sci Rep, vol. 3, no. 1, p. 1549, Dec 2013, doi: 10.1038/srep01549.

12. Briggs, N. et al. A roadmap for electronic grade 2D materials. *2D Mater.* 6 (no. 2), 022001 https://doi.org/10.1088/2053-1583/aaf836 (Jan. 2019).

13. Oh, J., Kim, Y., Chung, S., Kim, H. & Son, J. G. “Fabrication of a MoS$_2$/Graphene Nanoribbon Heterojunction Network for Improved Thermoelectric Properties,” Adv. Mater. Interfaces, p. 1901333, Oct 2019, doi: 10.1002/admi.201901333.

14. Erturk, A. & Inman, D. J. *Piezoelectric energy harvesting* (Wiley, Chichester, 2011).
15. Falconi, C. Piezoelectric nanotransducers. *Nano Energy.* **59**, 730–744 https://doi.org/10.1016/j.nanoen.2019.03.027 (May 2019).

16. Díaz-Sánchez, J. et al. “Complementary electrochromic devices of PANI and PEDOT using the enzymatic poly(gallic acid),” Solar Energy Materials and Solar Cells, vol. 200, p. 109973, Sep 2019, doi: 10.1016/j.solmat.2019.109973.

17. Martínez-Cisneros, E. et al. “Electromechanical Modeling of MEMS-Based Piezoelectric Energy Harvesting Devices for Applications in Domestic Washing Machines,” Energies, vol. 13, no. 3, p. 617, Feb 2020, doi: 10.3390/en13030617.

18. Caballero-Pérez, R. O., Bravo-Castillero, J., Pérez-Fernández, L. D., Rodríguez-Ramos, R. & Sabina, F. J. “Computation of effective thermo-piezoelectric properties of porous ceramics via asymptotic homogenization and finite element methods for energy-harvesting applications,” Arch Appl Mech, vol. 90, no. 6, pp. 1415–1429, Jun 2020, doi: 10.1007/s00419-020-01675-6.

19. Marchetti, L., Berg, Y., Mirmotahari, O. & Azadmehr, M. “Bidirectional front-end for piezoelectric resonator,” in 2016 *IEEE 13th International Conference on Networking, Sensing, and Control (ICNSC)*, Mexico City, Mexico, Apr. 2016, pp. 1–4, doi: 10.1109/ICNSC.2016.7479028.

20. Jaffe, B., Cook, W. R. & Jaffe, H. L. *Piezoelectric ceramics* (Academic Press, London, New York, 1971).

21. Aksel, E. & Jones, J. L. “Advances in Lead-Free Piezoelectric Materials for Sensors and Actuators,” Sensors, vol. 10, no. 3, pp. 1935–1954, Mar 2010, doi: 10.3390/s100301935.

22. Soergel, E. Piezoresponse force microscopy (PFM). *J. Phys. D: Appl. Phys.* **44** (no. 46), 464003 https://doi.org/10.1088/0022-3727/44/46/464003 (Nov. 2011).

23. Jungk, T., Hoffmann, Á. & Soergel, E. Quantitative analysis of ferroelectric domain imaging with piezoresponse force microscopy. *Appl. Phys. Lett.* **89** (no. 16), 163507 https://doi.org/10.1063/1.2362984 (Oct. 2006).

24. Sappati, K. & Bhadra, S. Piezoelectric Polymer and Paper Substrates: A Review. *Sensors.* **18** (no. 11), 3605 https://doi.org/10.3390/s18113605 (Oct. 2018).

25. Ahart, M. et al. “Origin of morphotropic phase boundaries in ferroelectrics,” *Nature*, vol. 451, no. 7178, pp. 545–548, Jan. 2008, doi: 10.1038/nature06459.

26. Guan, Z. et al. Identifying intrinsic ferroelectricity of thin film with piezoresponse force microscopy. *AIP Advances.* **7** (no. 9), 095116 https://doi.org/10.1063/1.4999199 (Sep. 2017).

27. Kholkin, A. L., Bdikin, I. K., Kiselev, D. A., Shvartsman, V. V. & Kim, S. H. “Nanoscale characterization of polycrystalline ferroelectric materials for piezoelectric applications,” *J Electroceram*, vol. 19, no. 1, pp. 83–96, Oct 2007, doi: 10.1007/s10832-007-9045-2.

28. Roelofs, A., Schneller, T., Szot, K. & Waser, R. Towards the limit of ferroelectric nanosized grains. *Nanotechnology.* **14** (no. 2), 250–253 https://doi.org/10.1088/0957-4484/14/2/328 (Feb. 2003).

29. Maldonado-Orozco, M. C. et al. Absence of ferromagnetism in ferroelectric Mn-doped BaTiO 3 nanofibers. *J Am Ceram Soc.* **102** (no. 5), 2800–2809 https://doi.org/10.1111/jace.16179 (May 2019).
30. Zúñiga, V. T., Carmona, S. G. & Morales Saavedra, O. G. Electromechanical characterization of didactical piezoelectric sensors based on crystalline grade PET. *J. Phys.: Conf. Ser.* **1221**, 012059 https://doi.org/10.1088/1742-6596/1221/1/012059 (Jun. 2019).

31. Zaki, A., Elsimary, H. & Zaghloul, M. “Miniature SAW device using MEMS technology,” *Microelectronics Journal*, vol. 38, no. 3, pp. 426–429, Mar 2007, doi: 10.1016/j.mejo.2006.11.010.

32. Rupitsch, S. J. *Piezoelectric Sensors and Actuators: Fundamentals and Applications* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2019).

33. Panda, P. K. Review: environmental friendly lead-free piezoelectric materials. *J Mater Sci.* **44**, 195049–195062 https://doi.org/10.1007/s10853-009-3643-0 (Oct. 2009).

34. Saito, Y. *et al.* “Lead-free piezoceramics,” *Nature*, vol. 432, no. 7013, pp. 84–87, Nov. 2004, doi: 10.1038/nature03028.

35. Damjanovic, D., Klein, N., Li, J., Porokhonskyy, V. & “WHAT CAN BE EXPECTED FROM LEAD-FREE PIEZOELECTRIC MATERIALS.,” *Funct. Mater. Lett.*, vol. 03, no. 01, pp. 5–13, Mar. 2010, doi: 10.1142/S1793604710000919.

36. Oh, H. & Dayeh, S. A. Physics-Based Device Models and Progress Review for Active Piezoelectric Semiconductor Devices. *Sensors* **20**, 143872 https://doi.org/10.3390/s20143872 (Jul. 2020).

37. Gullapalli, H. *et al.* “Flexible Piezoelectric ZnO-Paper Nanocomposite Strain Sensor,” *Small*, vol. 6, no. 15, pp. 1641–1646, Jul. 2010, doi: 10.1002/smll.201000254.

38. Banno, H. & Tsunooka, T. “Piezoelectric Properties and Temperature Dependences of Resonant Frequency of WO3 -MnO2 -Modified Ceramics of Pb(Zr-Ti)O3,” *Jpn. J. Appl. Phys.*, vol. 6, no. 8, pp. 954–962, Aug 1967, doi: 10.1143/JJAP.6.954.

39. Zong, X., Yang, Z., Li, H. & Yuan, M. “Effects of WO3 addition on the structure and electrical properties of Pb3O4 modified PZT–PFW–PMN piezoelectric ceramics,” *Materials Research Bulletin*, vol. 41, no. 8, pp. 1447–1454, Aug 2006, doi: 10.1016/j.materresbull.2006.02.002.

40. Zhong, N., Dong, X. L., Sun, D., Xiang, P. & Du, H. “Electrical properties of Pb(Mg1/3Nb2/3)O3–PbTiO3 ceramics modified with WO3,” *Materials Research Bulletin*, vol. 39, no. 2, pp. 175–184, Feb 2004, doi: 10.1016/j.materresbull.2003.10.007.

41. Slimani, Y. *et al.* Role of WO3 nanoparticles in electrical and dielectric properties of BaTiO3–SrTiO3 ceramics. *J Mater Sci: Mater Electron.* **31** (no. 10), 7786–7797 https://doi.org/10.1007/s10854-020-03317-7 (May 2020).

42. Chen, Y. *et al.* Polarization-Enhanced direct Z-scheme ZnO-WO3 – x nanorod arrays for efficient piezoelectric-photoelectrochemical Water splitting. *Appl. Catal. B.* **259**, 118079 https://doi.org/10.1016/j.apcatb.2019.118079 (Dec. 2019).

43. Corby, S., Francàs, L., Kafizas, A. & Durrant, J. R. Determining the role of oxygen vacancies in the photoelectrocatalytic performance of WO3 for water oxidation. *Chem. Sci.* **11** (no. 11), 2907–2914 https://doi.org/10.1039/C9SC06325K (2020).

44. Soltani, T., Tayyebi, A., Hong, H., Mirfasih, M. H. & Lee, B. K. “A novel growth control of nanoplates WO3 photoanodes with dual oxygen and tungsten vacancies for efficient photoelectrochemical water
splitting performance,” Solar Energy Materials and Solar Cells, vol. 191, pp. 39–49, Mar 2019, doi: 10.1016/j.solmat.2018.10.019.

45. Kim, Y., Alexe, M. & Salje, E. K. H. Nanoscale properties of thin twin walls and surface layers in piezoelectric WO3 – x. *Appl. Phys. Lett.* 96 (no. 3), 032904 https://doi.org/10.1063/1.3292587 (Jan. 2010).

46. Olivas-Ortega, D. E., Ramos-Cano, J., Talamantes-Soto, R. P., Lopez-Melendez, C. & Hurtado-Macias, A. “Nano-Mechanical and Piezoelectric Properties on PZT Thin Films,” *Microsc Microanal.* vol. 24, no. S1, pp. 2236–2237, Aug 2018, doi: 10.1017/S1431927618011662.

47. Mohanty, D. *et al.* “Synthesis and piezoelectric response of cubic and spherical LiNbO3 nanocrystals,” RSC Adv., vol. 2, no. 5, p 1913, 2012, doi: 10.1039/c2ra00628f.

48. Zúñiga, V. T., Carmona, S. G. & Morales Saavedra, O. G. Electromechanical characterization of didactical piezoelectric sensors based on crystalline grade PET. *J. Phys.: Conf. Ser.* 1221, 012059 https://doi.org/10.1088/1742-6596/1221/1/012059 (Jun. 2019).

49. Berak, J. M. & Sienko, M. J. Effect of oxygen-deficiency on electrical transport properties of tungsten trioxide crystals. *Journal of Solid State Chemistry.* 2 (no. 1), 109–133 https://doi.org/10.1016/0022-4596(70)90040-X (Jun. 1970).

50. Deb, S. K. Opportunities and challenges in science and technology of WO3 for electrochromic and related applications. *Solar Energy Materials and Solar Cells.* 92 (no. 2), 245–258 https://doi.org/10.1016/j.solmat.2007.01.026 (Feb. 2008).

51. Greiner, M. T., Chai, L., Helander, M. G., Tang, W. M. & Lu, Z. H. “Transition Metal Oxide Work Functions: The Influence of Cation Oxidation State and Oxygen Vacancies,” Adv. Funct. Mater., vol. 22, no. 21, pp. 4557–4568, Nov 2012, doi: 10.1002/adfm.201200615.

52. Koo, B. R. & Ahn, H. J. Fast-switching electrochromic properties of mesoporous WO3 films with oxygen vacancy defects. *Nanoscale.* 9, 451788–4517793 https://doi.org/10.1039/C7NR06796H (2017).

53. Lee, C. T. *et al.* “Investigation of Microstructure, Electrical and Optical Properties of WO3 Film by RF Magnetron Sputtering with Ar/H2,” AMR, vol. 123–125, pp. 983–986, Aug 2010, doi: 10.4028/www.scientific.net/AMR.123-125.983.

54. Lee, S., Yun, K. H. & Kim, D. Electroforming-less and multi-level resistive switching characteristics in tungsten oxide thin film. *Thin Solid Films.* 674, 91–96 https://doi.org/10.1016/j.tsf.2019.02.012 (Mar. 2019).

55. Sachs, M. *et al.* “Effect of oxygen deficiency on the excited state kinetics of WO3 and implications for photocatalysis,” *Chem Sci,* vol. 10, no. 22, pp. 5667–5677, Jun. 2019, doi: 10.1039/c9sc00693a.

56. Won, S., Lee, S. Y., Park, J. & Seo, H. Forming-less and Non-Volatile Resistive Switching in WOX by Oxygen Vacancy Control at Interfaces. *Sci Rep.* 7 (no. 1), 10186 https://doi.org/10.1038/s41598-017-10851-8 (Dec. 2017).

57. Manciu, F. S. *et al.* “Spectroscopic analysis of tungsten oxide thin films,” J. Mater. Res., vol. 25, no. 12, pp. 2401–2406, Dec 2010, doi: 10.1557/jmr.2010.0294.
58. Hamdi, H., Salje, E. K. H., Ghosez, P. & Bousquet, E. First-principles re-investigation of bulk WO3. *Phys. Rev. B.* 94, 24245124 https://doi.org/10.1103/PhysRevB.94.245124 (Dec. 2016).

59. Ramana, C. V., Utsunomiya, S., Ewing, R. C., Julien, C. M. & Becker, U. “Structural Stability and Phase Transitions in WO3 Thin Films,” J. Phys. Chem. B, vol. 110, no. 21, pp. 10430–10435, Jun 2006, doi: 10.1021/jp056664i.

60. Vemuri, R. S., Carbjbal-Franco, G., Ferrer, D. A., Engelhard, M. H. & Ramana, C. V. “Physical properties and surface/interface analysis of nanocrystalline WO3 films grown under variable oxygen gas flow rates,” Applied Surface Science, vol. 259, pp. 172–177, Oct 2012, doi: 10.1016/j.apsusc.2012.07.014.

61. Enriquez-Carrejo, J. L., Ramos, M. A., Mireles-Jr-Garcia, J. & Hurtado-Macias, A. Nano-mechanical and structural study of WO3 thin films. *Thin Solid Films.* 606, 148–154 https://doi.org/10.1016/j.tsf.2016.03.054 (May 2016).

62. Woodward, P. M., Sleight, A. W. & Vogt, T. “Ferroelectric Tungsten Trioxide,” Journal of Solid State Chemistry, vol. 131, no. 1, pp. 9–17, Jun 1997, doi: 10.1006/jssc.1997.7268.

63. Locherer, K. R., Swainson, I. P. & Salje, E. K. H. Transition to a new tetragonal phase of WO3: crystal structure and distortion parameters. *J. Phys.: Condens. Matter.* 11, 214143–214156 https://doi.org/10.1088/0953-8984/11/21/303 (May 1999).

64. Li, M. *et al.* Effect of hydrogen on the integrity of aluminium–oxide interface at elevated temperatures. *Nat Commun.* 8 (no. 1), 14564 https://doi.org/10.1038/ncomms14564 (Apr. 2017).

65. Sequeira, C. A. C., Rodrigues, L. F. F. T. G. & Santos, D. M. F. Cation Diffusivity in Nonstoichiometric Tungsten Trioxide Films. *ECS J. Solid State Sci. Technol.* 1 (no. 5), 136–139 https://doi.org/10.1149/2.010205jss (2012).

66. Kavitha, V. S. *et al.* “Tb3+-doped WO3 thin films: A potential candidate in white light emitting devices,” Journal of Alloys and Compounds, vol. 788, pp. 429–445, Jun 2019, doi: 10.1016/j.jallcom.2019.02.222.

67. Bose, R. J., Kavitha, V. S., Sudarsanakumar, C. & Pillai, V. P. M. Phase modification and surface plasmon resonance of Au/WO3 system. *Appl. Surf. Sci.* 379, 505–515 https://doi.org/10.1016/j.apsusc.2016.04.100 (Aug. 2016).

68. Ibrahim, A. B. M. A., Murgan, R., Abd Rahman, M. K. & Osm, J. “Morphotropic Phase Boundary in Ferroelectric Materials,” in Ferroelectrics - Physical Effects, M. Lallart, Ed. InTech 2011.

69. Boll, T., Unocic, K. A., Pint, B. A. & Stiller, K. “Interfaces in Oxides Formed on NiAlCr Doped with Y, Hf, Ti, and B,” Microsc Microanal, vol. 23, no. 2, pp. 396–403, Apr 2017, doi: 10.1017/S1431927617000186.

70. Thummavichai, K. *et al.* “Low Temperature Annealing Improves the Electrochromic and Degradation Behavior of Tungsten Oxide (WOx) Thin Films,” J. Phys. Chem. C, vol. 121, no. 37, pp. 20498–20506, Sep 2017, doi: 10.1021/acs.jpcc.7b06300.

71. Díaz-Reyes, J., Dorantes-García, V., Pérez-Benítez, A. & Balderas-López, J. A. “Obtaining of films of tungsten trioxide (WO3) by resistive heating of a tungsten filament,” p.6, 2008.
72. Gangwar, J., Gupta, B. K., Tripathi, S. K. & Srivastava, A. K. Phase dependent thermal and spectroscopic responses of Al2O3 nanostructures with different morphogenesis. *Nanoscale*. 7 (no. 32), 13313–13344 https://doi.org/10.1039/C5NR02369F (2015).

73. Kalantar-zadeh, K. et al. “Synthesis of Atomically Thin WO3 Sheets from Hydrated Tungsten Trioxide,” Chem. Mater., vol. 22, no. 19, pp. 5660–5666, Oct 2010, doi: 10.1021/cm1019603.

74. Horsley, J. A., Wachs, E., Brown, J. M., Via, H. & Hardcastlex, F. D. “Structure of Surface Tungsten Oxide Species in the WO/Al2O3 Supported Oxide System from X-ray Absorption Near-Edge Spectroscopy and Raman Spectroscopy,” p. 7.

75. Chen, P. W. et al. “Fast response of complementary electrochromic device based on WO3/NiO electrodes,” Sci. Rep., vol. 10, no. 1, p. 8430, Dec 2020, doi: 10.1038/s41598-020-65191-x.

76. Li, S., Yao, Z., Zhou, J., Zhang, R. & Shen, H. Fabrication and characterization of WO3 thin films on silicon surface by thermal evaporation. *Mater. Lett.* 195, 213–216 https://doi.org/10.1016/j.matlet.2017.02.078 (May 2017).

**Figures**

![Figure a) and b) images]

![Figure d) and e) images]

![Figure f) image]
Figure 1

a) Topography in contact mode of the representative sample WO3 thin film annealing at 400°C, b) and c) is the PFM Signal Phase before and after measurements the local hysteresis loops. d) Amplitude, e) phase, and f) piezo response (d33) versus AC Applied bias voltage of WO3 thin film annealed at 400°C.

Figure 2

Grazing incidence X-ray diffraction pattern for all as-deposited WO3 thin films over sapphire. GIXRD measurements were performed in samples annealed at 300 °C, 400 °C, 500 °C, 550 °C, and room-temperature as reference. The sample at 300 °C presents an amorphous structure, while 400 °C shows a mixture of cubic Al, monoclinic and tetragonal WO3 phases. Sample at 500 °C presents a mixture of monoclinic WO3 and cubic Al-WOx. Finally, the sample annealed at 550 °C consists of tetragonal WO3 and cubic Al-WOx phase. (It is possible to observe the evolution of crystallographic structures between $2\theta = 32^\circ$ and $46^\circ$ as indicated by orange dotted box).
Figure 3

A series of atom probe tomography with corresponding concentration profiles for 400 °C and 500 °C WO3-x thin films as-deposited over Al2O3 substrates. a) Sample annealed at 400°C where it is possible to observe some Al clusters (grey color indicated by the arrow). b) Sample annealed at 500°C with no traces of aluminum clusters. The composition profiles were created with a bin width of 2.5 nm and background corrected with IVAS 3.6.14 obtained along the long axis of the images corresponding to film growth direction.