Center for Energy Efficient Electronics Science

A National Science Foundation Science & Technology Center

Spray Pyrolyzed Lanthanum-doped Zirconia for Thin Film Transistor Applications

Ava Tan[1], William Scheideler[2], Vivek Subramanian[2]
[1]School of Electrical & Computer Engineering, Cornell University
[2]Department of Electrical Engineering & Computer Sciences, UC Berkeley

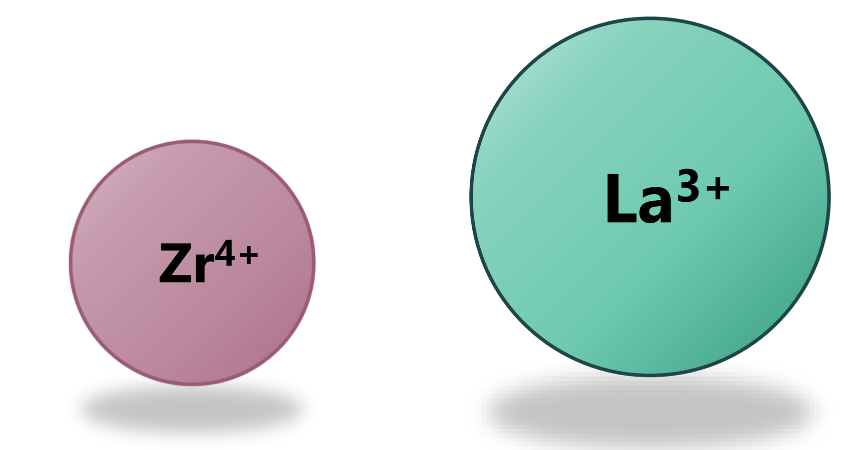
Abstract

High-κ metal oxides are being extensively investigated for use as viable gate dielectric materials to replace silicon dioxide (SiO_2) in thin film transistors. Composite materials such as lanthanum-doped zirconia ($La_xZr_{1-x}O_y$) are attractive options to explore, as a combination of materials with individually favorable qualities can yield dielectrics with large bandgaps and high dielectric constants. Alloyed dielectrics, remaining amorphous at high temperatures, also tend to be more resistant to crystallization, which can potentially reduce leakage currents when used in fabricated devices. Lanthanum, which has a slightly larger atomic radius than zirconium, acts as a deterrent for crystallization in zirconia films by inducing steric hindrance effects during film formation. Lanthanum-doped zirconia (LZO) films with varying lanthanum concentrations of 0, 2, 5, 10, and 20% were grown using an alternative solution-processing technique, spray pyrolysis, as a means of investigating a versatile, highly repeatable manufacturing mechanism to replace traditional vacuum-based techniques. The resulting films have high dielectric constants (~13-14), high breakdown fields (~3-4 MV/cm), and leakage current densities as low as 10^{-8} A/cm^2. Finally, metal oxide thin film transistors (TFTs) incorporating these dielectric films are fabricated and assessed for their electrical performance, as well as their potential for large-scale applications.

Introduction and Background

ZrO_2 demonstrates characteristics that make it one of the most promising materials to replace SiO_2. Properties such as a high dielectric constant κ ~ 10-23, a wide bandgap ~ 5.7 eV, and high optical transparency are amongst the many qualities that make ZrO_2 an attractive candidate as a gate dielectric for thin film transistors (TFTs) [1].

Additionally, it is desirable for the dielectric film to be relatively smooth and uniform to achieve a homogeneous electric field distribution as well as a better dielectric-semiconductor interface to minimize interfacial defects [2, 3]. Amorphous films lack grain boundaries which induce higher leakage current [2].



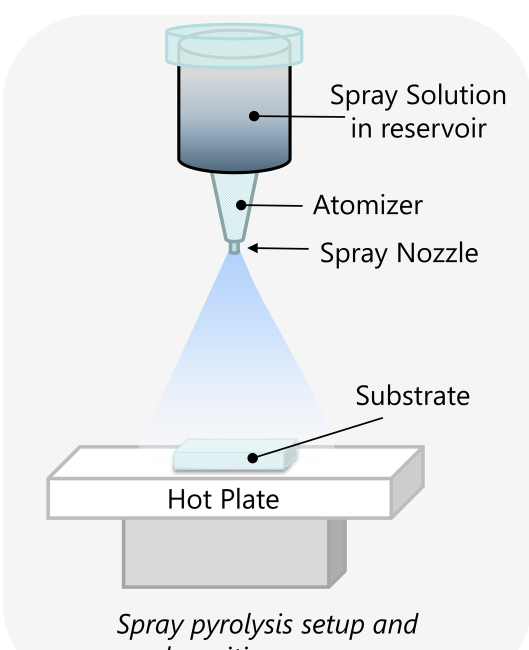
Zr radius ~ 127 pm. *La radius ~ 187 pm.*

A viable option for impeding crystallization in zirconium oxide is to alloy it with aliovalent La, which may reduce oxygen vacancies, an important defect in high-k dielectrics. Alloying and lower deposition temperatures preserve the amorphous nature of the resulting films [2].

Methods/Experimental Process

MIM Devices for LZO Characterization

Spray LZO Dielectric → Thermally evaporate Au contacts

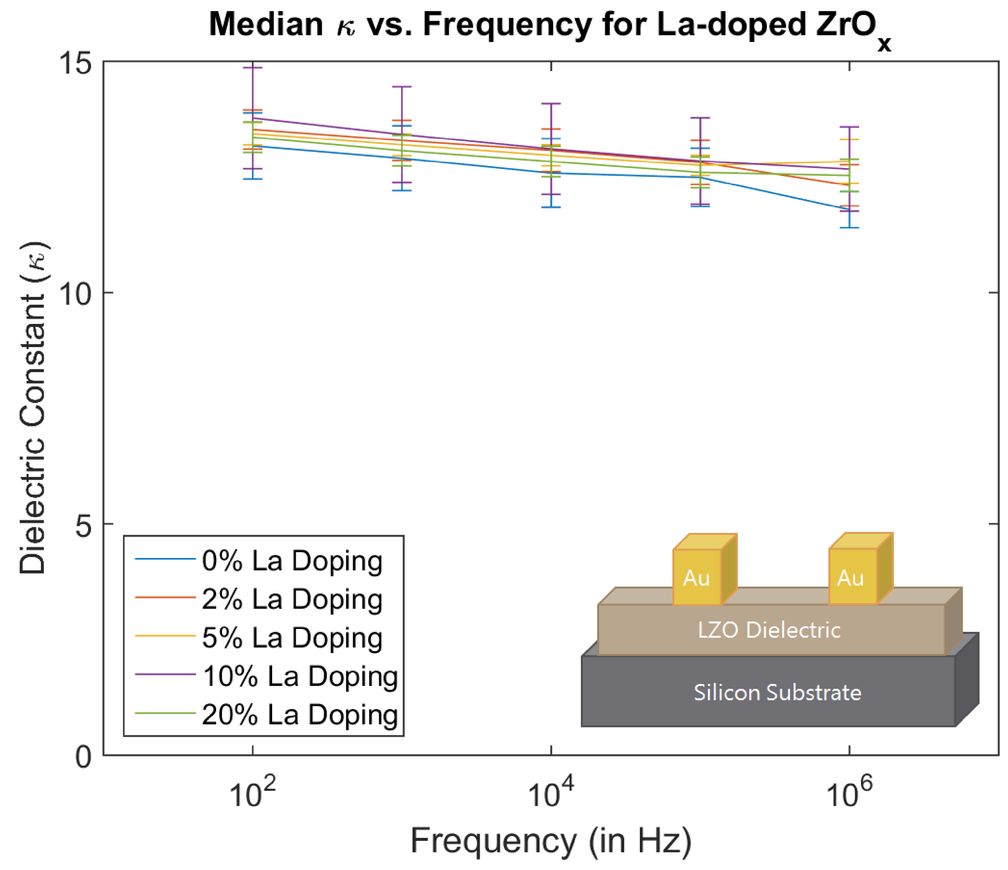


Spray pyrolysis setup and deposition process.

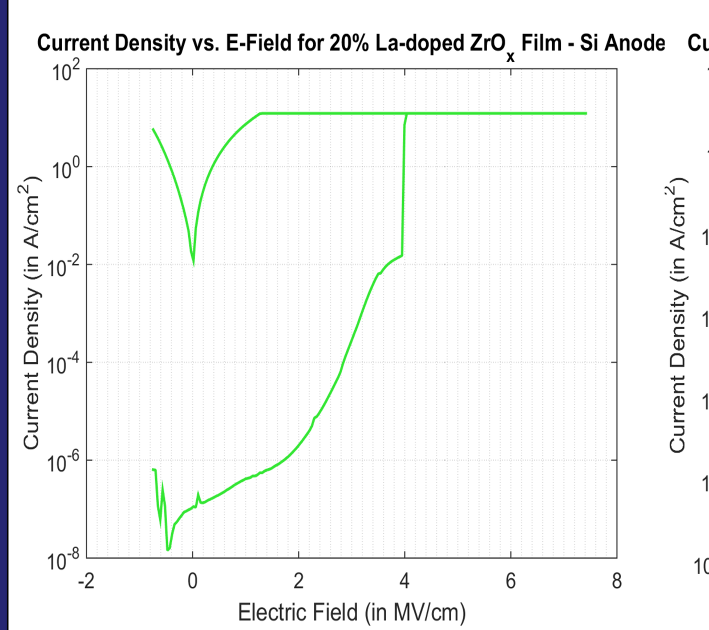
TFT Devices using LZO Dielectrics

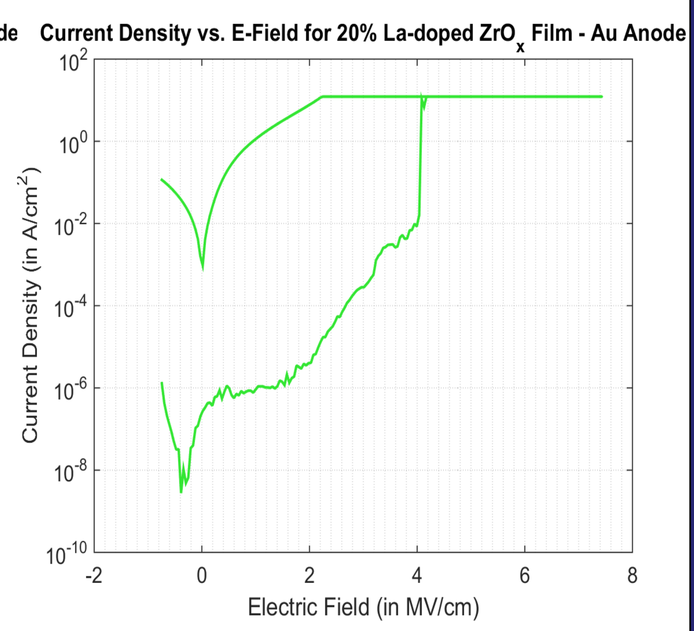
Spray LZO Dielectric → Spin-coat PMMA → Inkjet Print ATO → Anneal ATO contacts → Spray SnO_2 Semiconducting Channel

Results and Discussion



As little as 2% lanthanum doping can mitigate dielectric relaxation in pure zirconia. Lanthanum may stabilize the dielectric constant of zirconia, showing evidence of improving it at high frequencies (~ 1 MHz) for higher doping. Pure ZrO_X and LaO_x films have dielectric constants in the range of 10 – 20. The addition of LaO_x does not significantly alter the dielectric constant of the alloy films.





The resulting LZO films (for all lanthanum doping percentages) have thicknesses of 13-16 nm, breakdown fields of 3 – 4.5 MV/cm with evidence of the Fowler-Nordheim effect, and leakage currents of 10^{-8} – 10^{-6} A/cm^2. These values are competitive for dielectric films deposited by spray pyrolysis and are a testament to the yield for high-quality electronic films by this technique.

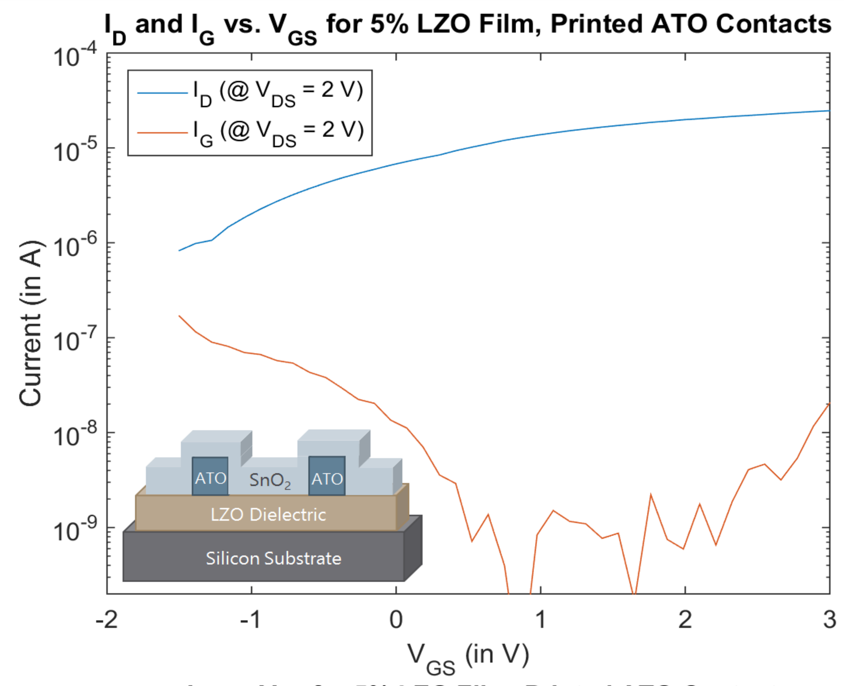
Conclusions and Future Work

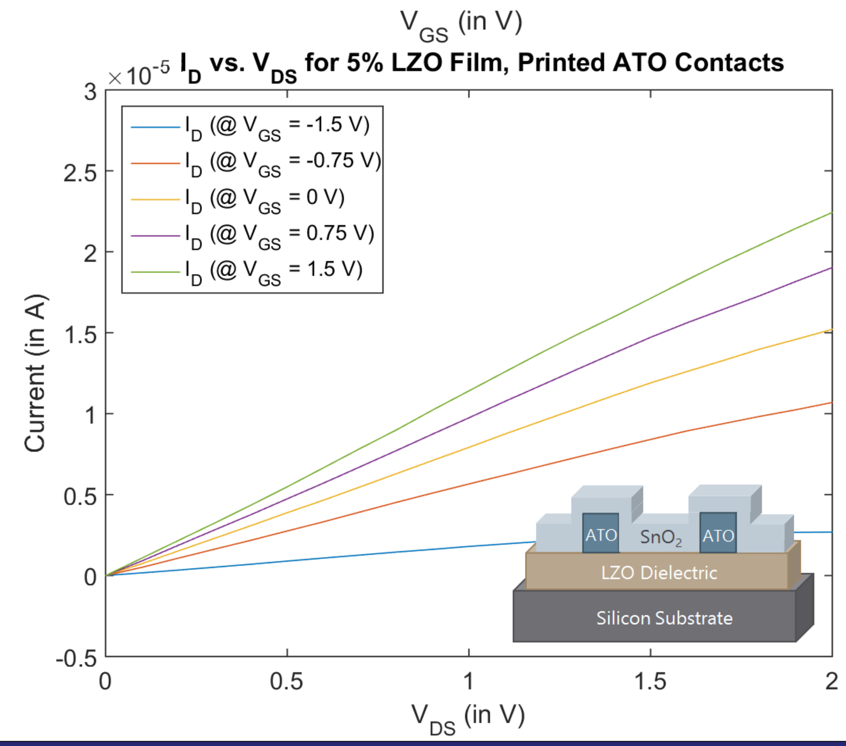
The primary purpose of this summer project is to characterize the dielectric properties, both from an electrical and materials perspective, of a specific spray pyrolyzed high-κ dielectric: lanthanum-doped zirconia (LZO). Thin film transistors incorporating LZO were made successfully, but the process by which TFTs are made using this particular dielectric material will benefit from further refining. The characterization of LZO will provide critical groundwork for future experimentation in TFT fabrication.

Ava Tan
Email: ajt222@cornell.edu
Phone: (219) 241-5289

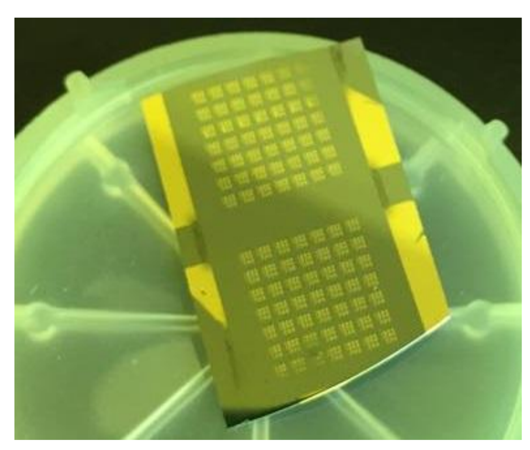
Support Information
This work was funded by National Science Foundation Award ECCS-0939514.

TFT Characteristics

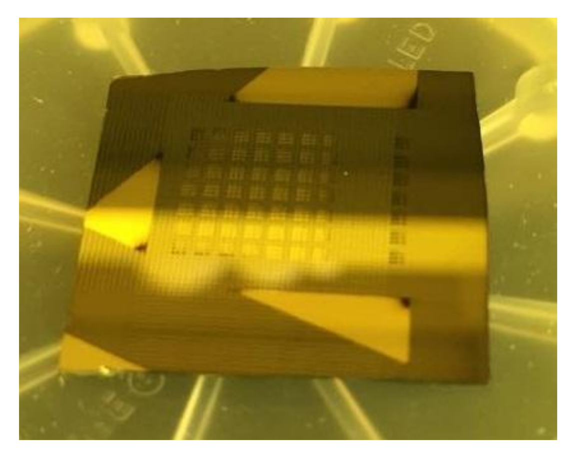




MIM/TFT Devices



MIM structures with LZO film and thermally evaporated gold contacts



TFT devices with LZO film, zinc oxide semiconductor and thermally evaporated aluminum contacts

Acknowledgements

I would like to thank Professor Vivek Subramanian for making this project possible and my mentor William Scheideler for his indispensable guidance and patience. I would also like to thank Carlos Biaou for his help regarding this project, as well as the Center for Energy Efficient Electronics Science for granting me this incredible opportunity to conduct research.

References

[1] Mazran Esro, George Vourlias, Christopher Somerton, William I. Milne, and George Adamopoulos. High-mobility ZnO thin film transistors based on solution-processed hafnium oxide gate dielectrics. *Advanced Functional Materials*, 25(1):134–141, 2015.

[2] Dennis M. Hausmann and Roy G. Gordon. Surface morphology and crystallinity control in the atomic layer deposition (ALD) of hafnium and zirconium oxide thin films. *Journal of Crystal Growth*, 249(12):251 – 261, 2003.

[3] Feng Xu, Ao Liu, Guoxia Liu, Byoungchul Shin, and Fukai Shan. Solution-processed yttrium oxide dielectric for high-performance IZO thin-film transistors. *Ceramics International*, 2015.