Final Technical Report

Dielectrics Under Extreme Electric Fields: *In Situ* Studies on Nanoscale Mechanisms

Award Number: DE−SC0017839

Total budget: $674,999

Period of performance: 09/15/2017 – 7/14/2020 (with no-cost-extension to 7/14/2022)

Xiaoli Tan, PI, Iowa State University

Geoff Brennecka, co-PI, Colorado School of Mines

Accomplishments

1. Major goals of the project

The lack of materials that can function reliably under extreme electric fields is a critical roadblock to achieving higher energy efficiency and extended service lifetime of devices in electricity generation, transmission, and consumption. Materials typically fail at two or three orders of magnitude below their theoretical dielectric breakdown strength. Identifying the origins of premature dielectric breakdown using state-of-the-art characterization tools will, therefore, enable the design and discovery of transformational materials capable of approaching their intrinsic limits. The vast improvement in the resolution power of imaging tools, combined with the recently developed *in situ* electric biasing technique, has made high resolution observations of dielectric breakdown as it happens possible. The overall goal of the project is to directly image the dynamic processes of defect formation, accumulation, and interaction with pre-existing defects (e.g., dislocations, domain walls, and grain boundaries in crystalline dielectric films) under electric fields up to 1,000 MV/m with a temporal resolution better than 5 microseconds. Using the newly acquired, custom-made Hysitron PI95 transmission electron microscopy (TEM) specimen holder, *in situ* TEM observations of breakdown at the sub-nanometer resolution will be made on representative dielectric compounds with progressive complexities: the linear dielectric SiO_2, CuO, and TiO_2, the ferroelectric $BaTiO_3$ nanocrystals and nanocubes. Through direct observation of the breakdown event at high spatial and temporal resolutions, the nanoscale mechanisms for the failure of dielectrics under intense electric fields will be identified. The results of the project will be applied to the design and processing of new dielectric materials with higher efficiency, improved reliability, and a prolonged lifetime. Such new dielectrics are urgently needed for modernizing energy infrastructures.

2. Tasks accomplished

- The PI installed and tested the PI-95 specimen holder on the Tecnai TEM at the Sensitive Instrument Facility at the U.S. DOE Ames Laboratory.
- The co-PI has prepared high-quality TiO_2, CuO, and PZT films on the small Si-wedge substrate. The non-planar nature of the substrate makes the processing quite challenging. The sample configuration has been redesigned and films were fabricated using the dip-coating method with a conductive $LaNiO_3$ buffer layer. The co-PI has also attempted alternative approach by depositing TiO_2 and CuO directly on the W probe tip.
- *In situ* TEM experiments have been carried out on the Si wedge substrate with a native SiO_2 film. We directly observed the amorphization of Si single crystal under electric bias in the contiguous region of its native oxide layer. We further showed that the amorphized Si can be recrystallized under a bias of reversed polarity. Electron energy loss spectroscopy and energy dispersive X-ray spectroscopy analyses indicate that the amorphization and recrystallization of the crystalline Si is a result of directional migration of oxygen which originally comes from its native oxide layer. The findings are reported in *Journal of Applied Physics*.
- *In situ* TEM experiments are employed to characterize the structural and compositional changes of amorphous TiO_2 under extreme electric field (~100 kV/mm) in a $Si/TiO_2/W$ system. Upon applying voltage pulses, the amorphous TiO_2 gradually transformed to

crystalline sub-stoichiometric rutile TiO_{2-x} and the Magnéli phase Ti_3O_5. The transitions started from the anode/oxide interface under both field polarities. Preferred growth orientation of rutile TiO_{2-x} with respect to the Si substrate was observed when Si was the anode, while oxidation and melting of the W probe occurred when W was the anode. We associate the TiO_2 crystallization process with the electrochemical reduction of TiO_2, polarity-dependent oxygen migration, and Joule heating. The experimental results are supported by our phase-field modeling. These findings provide direct details of the defect formation process during dielectric breakdown in amorphous oxides and will help the design of electronic devices with higher efficiency and reliability. The results are reported in *ACS Applied Materials & Interfaces*.

- *In situ* TEM experiments have been conducted to show distinctly different defect-related and intrinsic breakdown processes in individual, single crystalline TiO_2 nanoparticles. As the applied electric field intensity rises, rutile-to-anatase phase transition, local amorphization/melting, or ablation are identified as the corresponding breakdown processes, the field intensity thresholds of which are found to be related to the position of the intensified field and the duration of the applied bias relative to the time of charged defects accumulation. Our observations reveal an intensity-dependent dielectric response of crystalline oxides at breakdown and suggest possible routes to suppress the initiation of premature dielectric breakdown. Hence, they will aid the design and development of next generation robust and efficient solid dielectrics. The results are reported in *ACS Nano*.
- *In situ* TEM experiments are carried out on two types of copper oxides (CuO and Cu_2O) to reveal the structural and electrical property changes under voltage bias. In both types of oxides, dynamic conductive path formation and dissolution are observed. The decrease in resistance of CuO film is found to be accompanied with the formation of Cu_4O_3 phase where the electric field strength is highest. We also find that the decrease in resistivity of Cu_2O film is more extensive and occurs in an area depending on the level of current compliance. The physical mechanisms responsible for the observations and their implications for the formation of conducting regions in copper oxide-based memristors are discussed. The results are reported in *IEEE Transactions on Devices and Materials Reliability*.
- *In situ* TEM experiments are conducted on $BaTiO_3$ perovskite nanocrystals. We discovered that formation of oxygen vacancies due to electrical stressing renders the oxide amorphizable under electron beam illumination, suggesting the presence of a threshold concentration of oxygen vacancy affecting the structural stability of $BaTiO_3$ crystals upon high energy radiation. In contrast to the structural change, the resistivity of the nanocrystal seems not liable to the amorphization prior to dielectric breakdown at higher voltage bias. We propose that an increase in oxygen vacancy content promotes oxygen mobility in the perovskite structure allowing electron beam induced electric field to modify the local structural and composition. Our *in-situ* observations reveal the central role of oxygen vacancies in the structural stability of perovskites which is of paramount importance to their applications in extreme environments and suggest a potential new route to micro-processing perovskite oxides using the electron beam via oxygen vacancy management without severely compromising the electric property. The results are reported in *Advanced Functional Materials*.

- *In situ* TEM experiments are conducted on individual pristine and doped $BaTiO_3$ nanocubes to measure their electrical properties. The dimensions of the nanocubes tested are between 10 and 20 nm. We characterized 4%Cr and 5%La doped $BaTiO_3$ nanocubes and compared them with the properties of pristine $BaTiO_3$ nanocubes. We found that the resistance of all three types of nanocubes when displayed in log-scale show a nearly linear dependence on the applied electric field over a wide range of electric fields (50 – 900 kV/cm). Compared with pristine $BaTiO_3$ nanocubes, the resistance of both 4%Cr and 5%La doped nanocubes showed reduced variation rates with respect to the electric field, with 5%La doping demonstrating a better reduction in the variation rate. By developing techniques capable of evaluating the properties of individual $BaTiO_3$ nanocubes, we expect that our work to open the door to the use of $BaTiO_3$ nanomaterials in the design of future ferroelectrics-enabled nanodevices with novel functionality. The results are reported in *Applied Physics Letters*.

3. Training and professional development opportunities

- Two postdocs, Dr. Joshua Hoemke and Dr. Xinchun Tian, have been trained to operate the transmission electron microscope and the most critical PI-95 picoindentor with electrical characterization module. Both of them have accumulated extensive experiences with *in situ* biasing TEM techniques and deep understanding of nanoscale mechanisms of dielectric breakdown.
- One M.S. student, Ms. Chloe Cook, was fully supported and one Ph.D. student, Ms. Valerie Jacobson, was partially supported by this project. Both were trained on solution process of thin films and produced TiO_2, CuO, and $Pb(Zr,Ti)O_3$ films on Si narrow wedge substrates. They also acquired general knowledge on ceramic synthesis and microelectronics technologies.

4. Research findings dissemination

- The research findings of this project were reported in six articles published in top-rated technical journals, including *Advanced Functional Materials* (Impact factor 19.92) and *ACS Nano* (Impact factor 15.88).
- The results were presented at the MRS 2020 Spring Meeting and the Materials Science and Technology 2020 Annual Meeting.
- The project has been featured in the Iowa State University College of Engineering Spring 2019 Research Magazine.

Products

1. Publications:

- X.C. Tian, T. Ma, L. Zhou, G. Brennecka, and X. Tan, *In situ* TEM study of the transitions between crystalline Si and nonstoichiometric amorphous oxide under bipolar voltage bias. ***Journal of Applied Physics*** 125, 245304 (2019). DOI: 10.1063/1.5100310.

- X.C. Tian, C. Cook, W. Hong, T. Ma, G. Brennecka, and X. Tan, *In situ* TEM study of the amorphous-to-crystalline transition during dielectric breakdown in TiO_2 film. ***ACS Applied Materials & Interfaces*** 11, 40726-40733 (2019). DOI: 10.1021/acsami.9b08146.
- X.C. Tian, G. Brennecka, and X. Tan, Direct observations of dielectric breakdown in TiO_2 single nanocrystals. ***ACS Nano*** 14, 8328-8334 (2020). DOI: 10.1021/acsnano.0c02346.
- X.C. Tian, S. Yazdanparast, G. Brennecka, and X. Tan, *In situ* TEM study of dielectric breakdown in copper oxides. ***IEEE Transactions on Devices and Materials Reliability*** 20, 609-612 (2020). DOI: 10.1109/TDMR.2020.3015398.
- X.C. Tian, G. Brennecka, and X. Tan, Structural instability in electrically stressed, oxygen deficient $BaTiO_3$ nanocrystals. ***Advanced Functional Materials*** 30, 2004607/1-9 (2020). DOI: 10.1002/adfm.202004607.
- X.C. Tian, G. Caruntu, B. Kavey, and X. Tan, *In-situ* TEM measurement of electrical properties of individual $BaTiO_3$ nanocubes. ***Applied Physics Letters*** 118, 192901/1-5 (2021). DOI: 10.1063/5.0049477.

2. Techniques:

- An *in situ* TEM technique for studying dielectric breakdown nanoscale mechanisms is developed.

Participants

Xiaoli Tan, PI. Email: xtan@iastate.edu; Phone: 515-294-3355
Contributions: Oversees the project; advises the postdocs; conducts regular research progress meetings; revises manuscripts; reports to sponsoring agency.

Geoff Brennecka, co-PI. Email: gbrennec@mines.edu
Contributions: Oversees the film deposition process, advises the graduate students, analyzes data and revises manuscripts.

Xinchun Tian, postdoc
Contributions: Prepares samples; performs the *in situ* TEM experiments; analyzes data; drafts/revises manuscripts for publication.

Joshua Hoemke, postdoc
Contributions: Prepares samples; performs the *in situ* TEM experiments; analyzes data.

Chloe Cook, M.S. student
Contributions: fabricates TiO_2, $Pb(Zr,Ti)O_3$, and $PbZrO_3$ thin films on the Si wedge substrate.

Valerie Jacobson, Ph.D. student
Contributions: fabricates CuO and $Pb(Zr,Ti)O_3$ thin films.