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Manufacturing Steps for Commercial Production of Nano-Structure Capacitors Final Report CRADA No. TC02159.0

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Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Manufacturing Steps for Commercial Production of Nano-Structure Capacitors

Final Report
CRADA No. TC02159.0
Date Technical Work Ended: December 30, 2012

Date: April 19, 2013 Revision: 2

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and TroyCap LLC.

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B. Project Scope

This was a collaborative effort between Lawrence Livermore National Security, LLC as manager and operator of Lawrence Livermore National Laboratory (LLNL) and TroyCap LLC, to develop manufacturing steps for commercial production of nano-structure capacitors.

The technical objective of this project was to demonstrate high deposition rates of selected dielectric materials which are 2 to 5 times larger than typical using current technology.

This project was originally designated as a six (6) month project, consisting of four (4) major tasks and the following four (4) major deliverables:

Deliverable 1: Design review meeting (LLNL/TroyCap) Due at the end of week 5.
Deliverable 2: Subsystem review meeting (LLNL/TroyCap) Due at the end of week 5
Deliverable 3: System Demonstration meeting (LLNL/TroyCap) Due at the end of week 9

Deliverable 4: Final Report and Abstract due within thirty (30) days of completion or termination of the project, as required under Article XI of the CRADA. (LLNL/TroyCap) Due 30 days after completion of CRADA

On 6/10/10 Amendment One was executed to add Participant funds-in to cover the costs required to complete the tasks and deliverables. On 9/24/10 a No-Cost Time Extension (NCTE) request was executed to extend the project by six months to allow enough time to complete the tasks and deliverables associated with the CRADA Statement of Work. The CRADA expiration date was extended to 3/31/11. On 12/2/10 Amendment Two was executed to revise Appendix D to add LLNL Background Intellectual Property.

Amendment Three, executed on 4/10/11, extended the term of the CRADA for an additional six (6) months, to September 30, 2011; modified Appendix D, added an additional task and deliverable; and increased the Participant's funds-in to cover the cost of the effort required to complete the following new task and deliverable.

Task 5: LLNL will fabricate ZrO_2 capacitor dielectric. Begin discussions with Innovative Systems Engineering, Inc. regarding design requirements for a sputtering tool that will be capable of making the capacitors. (LLNL)
Duration: 3 Months

Deliverable 5: ZrO_2 capacitor dielectric (LLNL) with the following specifications:

- $k = 24.5$ to 25
- $V_b > 4.0 \times 10^6$ V/cm

Capacitors – Area > 0.8 cm^2

- Capacitance ≈ 8 Nano Farads
- Yield > 70 %
- Single ZrO_2 dielectric layer
- Three (3) processing runs demonstrating reproducibility

On 8/12/11 a second NCTE request was executed, extending the expiration date of the CRADA for an additional six (6) months, to March 30, 2012, to allow enough time to complete the tasks and deliverables. A third NCTE request was executed on 4/24/12, extending the expiration date of the CRADA for three (3) months, to June 30, 2012 to allow enough time to complete the tasks and deliverables. A fourth NCTE request was executed on 8/8/12, extending the CRADA for six (6) months, to 12/20/12, to allow enough time to complete the final task and deliverable. Amendment Four, executed on November 26, 2012, modified Appendix D; all other terms and conditions remained the same.

All of the tasks for this project were successfully completed. Deliverable 5, ZrO_2 dielectric capacitor with an area > 0.8 cm^2, was not met due to unexpected technical limitations and limitations of available funding.

C. Technical Accomplishments

The technical objective of this project was to demonstrate high deposition rates of selected dielectric constant materials that are 2 to 5 times larger than typical using existing technology by means of a unique approach to the implementation of standard materials fabrication technologies. This has been demonstrated with the dielectric materials Zirconium Dioxide (ZrO_2; k – 29) and Tantalum Pent-oxide (Ta_2O_5; k = 26). Performance of ZrO_2 dielectric capacitors was quantitatively evaluated and experimentally determined to be in accord with measurements reported by prior investigators who implemented standard technologies. LLNL disclosed a Subject Invention resulting from this CRADA on 7/21/2011.

The specific technical accomplishments were:

1) Development of a conceptual approach to increasing the deposition rates of selected dielectric materials that are 2 to 5 times larger than typical using current industrial technology.

2) Design and implementation of modifications to an existing nano-laminate and multilayer materials magnetron sputter deposition system to implement the conceptual approach developed in 1).

3) Experimental demonstration of the increased sputter deposition rate of the dielectric ZrO_2 was generated. Two specific technological advances were implemented. First, an atomic oxygen source was used to oxidize thin (≈ 0.25 nm thick) Zr layers when operating in the separation of function mode. Second, substrates were sequentially exposed to the Zr metal sputter source and the atomic oxygen source thirty times a minutes sequentially fabricating thirty ZrO_2 layers 0.4 nm thick per minute on to substrates having an area of >150 in^2. A typical fixed substrate area used in refractory oxide synthesis for capacitor applications is ≈ 12 in^2 and a typical ZrO_2 fixed substrate deposition rate is ≈ 0.4 nm/second 24 nm /min.

   The increased moving substrate area is 12.5 the fixed substrate area. The deposition rate is 0.4 nm per substrate rotation or 12 nm/min for the moving substrates. This rate is multiplied by 12.5 to estimate an effective deposition rate on a static 12.5 in^2 area substrate. This results in an effective rate of 150 nm/min, a factor of six (6) greater than the static substrate deposition rate. This increase can be made larger by rotating at 60 rpm so the increase in deposition rate is then a factor of eighteen (18).

4) Monoclinic structure ZrO_2 for capacitors having an area of 3.5 x 10^{-3} cm^2 and dielectric thicknesses of 408 nm, 913 nm, 1400 nm, 1939 nm and 3915 nm were fabricated and tested. Breakdown fields were observed to be 2.9 MV/cm with a yield of greater than 78% of the capacitors fabricated. This breakdown is consistent with estimates for monoclinic structure ZrO_2 capacitor dielectric material. Extension of this result to a capacitor with dielectric area > 0.8 cm^2 was not achieved due to technical limitations.

D. Expected Economic Impact

The capacitor industry has a financial magnitude of $15,000,000,000 per year worldwide. This financial estimate does not include internally manufactured capacitor costs for equipment manufacturers. The "separation of function" approach, when successfully introduced into the market place, will be to enable enhanced, efficient electrical power control circuitry, increase the power utilization efficiencies for both hybrid and all electric power vehicles, enable new applications of high energy plasmas in oil and geothermal energy well digging, enhance the performance of dry-fracking natural gas recovery, increase the safety of high energy weapons and their effectiveness, and impact industry at the most fundamental levels. There will be new technologies based on the capacitor components manufactured the impact of which on employment is currently not known.

D.1 Specific Benefits

Benefits to DOE

This CRADA benefits DOE through the high-energy density capacitors that are both a vital component and an enabling technology for temporary energy storage and in electronic systems of all types. Nano-structure multilayer capacitors (NMC) offer a potential size and weight reduction to 0.01 of that available in present volume capacitor manufacturing technology. The potential reliability of the NMC is equivalent to that attained in present day very-large-scale-integration (VLSI) semiconductor technology.

These NMC capacitors will support a very broad range application profile as a result of:

- Application of linear dielectric materials represented in this CRADA by ZrO_2
- The low temperature dependencies of the dielectric constants for linear dielectric materials allowing operation over an extended temperature range
- Demonstrated synthesis of the linear dielectric ZrO_2 with upper limits for performance – breakdown fields and leakage – determined by intrinsic material crystal structure capabilities and not by manufacturing introduced imperfections. This will enable high breakdown fields minimizing the needed dielectric volume increasing manufacturability
- Synthesis of capacitor structures having high breakdown voltage thus high-energy storage. The upper limit for the energy stored in a capacitor is directly proportional to the square of the highest operational voltage capability.

Benefits to Industry

TroyCap and industry benefit through the resulting cost reduction from using efficiencies of scale from VLSI techniques and cluster tools for high volume production that has been projected to be on the order of less than 50% of present day volume manufactured capacitors. The LLNL developed NMC technology has further advantages in that it can be highly integrated with other electronic components on the same substrate, driving up reliability and driving down end-product costs. It additionally has the possibility to fabricate high performance very large capacitor structures.

E. Partner Contribution

As a result of the work conducted during the course of the collaboration, TroyCap evolved its ideas regarding potential market applications. We are currently discussing the market readiness of these applications and TroyCap is pursuing funding.

TroyCap considers that the deliverables have been met, and as a result, TroyCap intends to initiate a new CRADA with Lawrence Livermore National Lab to produce working single layer capacitors to be used in solid state pulse power modules for application in clean burning coal, solid state ignition systems and transient plasma hard rock drilling. Once the new CRADA produces functioning capacitors, TroyCap will commence production of these capacitors, in large quantities.

TroyCap created no subject based inventions during this CRADA.

F. Documents/Reference List

Reports

(Rough Draft Interim Report)
CRADA TC02159.0 "Manufacturing Steps for Commercial Production of Nano-Structure Capacitors", January 19, 2011, Troy W. Barbee, Jr.

An Interim in-depth DRAFT Technical Report was prepared in January 18, 2011 and presented in progress meetings with TroyCap representatives on the 19th of that month. This in-depth technical report is under preparation by Troy Barbee and will be available by March 30, 2013.

Copyright Activity
No Copyright Activity took place on this CRADA

Subject Inventions
LLNL disclosed the following Subject Invention resulting from this CRADA on 7/21/11:

IL12460A: patent pending

TroyCap LLC has expressed an interest in licensing this Subject Invention.

Background Intellectual Property
LLNL disclosed the following Background Intellectual Property for this project:

IL11909A: Patent pending

U.S. Patent No. 5,414,588 (LLNL Docket IL09103A) – *High Performance Capacitors Using Nano-Structure Multilayers Materials Fabrication*; Inventors: Troy W. Barbee, Jr., Gary W. Johnson, Dennis W. O'Brien

U.S. Patent No. 5,486,277 (LLNL Docket IL09103B) – *High Performance Capacitors Using Nano-Structure Multilayers Materials Fabrication*; Inventors: Troy W. Barbee, Jr., Gary W. Johnson, Dennis W. O'Brien

U.S. Patent No. 6,380,627 (LLNL Docket IL09615A) – *Low Resistance Barrier Layer for Isolating, Adhering, and Passivating Copper Metal in Semiconductor Fabrication*; Inventors: Timothy P. Weihs, Troy W. Barbee, Jr.

U.S. Patent No. 6,339,020 (LLNL Docket IL09615B) – *Method for Forming a Barrier Layer*; Inventors: Timothy P. Weihs, Troy W. Barbee, Jr.

U.S. Patent No. 5,731,538 (LLNL Docket IL09891A) – *Method and System for Making Integrated Solid State Fire-Sets and Detonators*; Inventors: Dennis W. O'Brien, Troy W. Barbee, Jr., Robert L. Druce, Gary W. Johnson, Ronald S. Lee

U.S. Patent No. 5,742,471 (LLNL Docket IL09901A) – *Nanostructure Multilayer Dielectric Materials for Capacitors and Insulators*; Inventors: Gary W. Johnson, Troy W. Barbee, Jr.

TroyCap has not expressed an interest in obtaining a license for the above LLNL Background Intellectual Property.

TroyCap LLC did not disclose any Background Intellectual Property for this project.

G. Acknowledgement

Industrial Participant's signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures generated by his/her respective company and attributable to the project have been disclosed and included in Section E or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

5-20-13
David Schena, Vice President Finance — Date
TroyCap LLC

6-27-13
Troy W. Barbee, LLNL Principal Investigator — Date
Lawrence Livermore National Laboratory

7/3/2013
~~Veronica Lanier, Acting Technology Commercialization Manager~~ — Date
Lawrence Livermore National Laboratory
Richard Rankin, Director - Industrial Partnership Office

Attachment I – Final Abstract

Manufacturing Steps for Commercial Production of Nano-Structure Capacitors

Final Abstract (Attachment I)
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E. Project Dates

March 31, 20120 to December 30, 2012