REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
16-11-2018	Final Report	23-Jun-2014 - 22-Jun-2016

4. TITLE AND SUBTITLE
Final Report: Nb/NbOx Metal-Insulator-Based Microrectenna Research (collaboration with US Army NSRDEC)

5a. CONTRACT NUMBER
W911NF-14-1-0320

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

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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)
65686-CH.2

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Ryan OHayre
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RPPR Final Report
as of 21-Nov-2018

Agency Code:

Proposal Number: 65686CH | **Agreement Number: W911NF-14-1-0320**

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DUNS Number: 010628170 | EIN: 846000551
Report Date: 22-Sep-2016 | Date Received: 16-Nov-2018
Final Report for Period Beginning 23-Jun-2014 and Ending 22-Jun-2016

Title: Nb/NbOx Metal-Insulator-Based Microrectenna Research (collaboration with US Army NSRDEC)

Begin Performance Period: 23-Jun-2014 | **End Performance Period:** 22-Jun-2016
Report Term: 0-Other
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 1

Major Goals: The goal of this project is to investigate the materials science of Nb/NbOx bilayers as substrates for MIM (metal-insulator-metal) diodes, where NbOx consists of 3-5 nm self-limiting native niobium oxide plus a precisely-controlled thickness of Nb2O5. The proposed bilayers will be also be investigated by our collaborators (US Army NSRDEC and MIT Lincoln Laboratory), who study the device physics and materials science of MIM diodes.

To understand structure-performance relationships, a variety of bilayer samples with different thickness and/or interfacial parameters will be fabricated and tested. Our development of the anodic oxidation technique for Nb/NbOx bilayer synthesis provides the control needed for these careful structural studies.

The quality of the Nb/NbOx interface and the number of defects in the NbOx layer are believed to be key determinants of diode performance. We will deposit Nb metal films on oxidized Si wafer substrates by DC magnetron sputtering and then subsequently treat by anodic oxidation to produce a highly-reproducible NbOx oxide film of tunable thickness. A series of samples with anodized oxide thicknesses of 10-20nm will be produced. Because the Nb metal layer possess a self-limiting native NbOx oxide film of ~3-5nm, the actual thickness of (NbOx+ Nb2O5) will be somewhat larger than the anodized Nb alone – so ~10-20 nm plus 3-5 nm native oxide will result in ~15-25 nm oxide coatings assuming a native oxide of 3-5 nm thickness. Electron microscopy will be employed to examine the Nb/NbOx bilayers. A focused-ion beam (FIB) will be used to prepare TEM lift-out sections of the Nb/NbOx bilayers, which will be examined via high-resolution TEM. We will correlate the structure of the interface (smoothness, defect density, relative crystalline vs. amorphous fraction of the oxide) to MIM performance.

Our high-quality Nb “ground planes” will provide an ideal test of MIM performance since they permit variation in the top metal (antenna size, shape, and perhaps even material), while keeping the bottom metal fixed. At the same time, the MIM diodes and related test structures will allow us to learn more about the NbOx films (e.g., barrier height, thickness, roughness, defects, etc.).

Accomplishments: See attached PDF report

Training Opportunities: PhD student Daniel Clark (partially supported under this grant) successfully graduated with his PhD in 2016.

Results Dissemination: All produced samples were sent to our collaborators at US Army NSRDEC. All TEM analyses and Nb/NbOx thickness measurements were also summarized in PPT presentations and shared with our NSRDEC collaborators. A joint paper was also published as a result of this work. The citation is provided below:

R. Osgood III, S. Giardini, J. Carlson, P. Periasamy, H. Guthrey, R. O'Hayre, M. Chin, B. Nichols, M. Dubey, G. E. Fernandes, J. H. Kim, J. Xu, P. Parilla, J. Berry, D. Ginley, "Conduction and rectification in NbOx- and NiO-based metal-insulator-metal diodes", J. Vac. Sci. and Tech. A., 34(5), 051514 (2016) DOI: 10.1116/1.4960962

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: All samples as well as the method of bilayer production we have developed in this project were transferred to our US NSRDEC partners.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Ryan O'Hayre
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Joghee Prabhuram
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Daniel Clark
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

RPPR Final Report
as of 21-Nov-2018

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films
Publication Identifier Type: DOI Publication Identifier: 10.1116/1.4960962
Volume: 34 Issue: 5 First Page #: 051514
Date Submitted: Date Published: 9/1/16 6:00AM
Publication Location:

Article Title: Conduction and rectification in NbOx- and NiO-based metal-insulator-metal diodes

Authors: Richard M. Osgood, Stephen Giardini, Joel Carlson, Prakash Periasamy, Harvey Guthrey, Ryan O'Hayr

Keywords: rectenna, light rectification, solar harvesting

Abstract: Conduction and rectification in nanoantenna-coupled NbOx- and NiO-based metal-insulator-metal (MIM) diodes (“nanorectennas”) are studied by comparing new theoretical predictions with the measured response of nanorectenna arrays. A new quantum mechanical model is reported and agrees with measurements of current–voltage (I–V) curves, over 10 orders of magnitude in current density, from [NbOx(native)-Nb2O5]- and NiO-based samples with oxide thicknesses in the range of 5–36 nm. The model, which introduces new physics and features, including temperature, electron effective mass, and image potential effects using the pseudobarrier technique, improves upon widely used earlier models, calculates the MIM diode’s I–V curve, and predicts quantitatively the rectification responsivity of high frequency voltages generated in a coupled nanoantenna array by visible/nearinfrared light.

Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Nb/NbO_x metal-insulator-based microrectenna research (collaboration with US Army NSRDEC)

PI: Ryan O'Hayre, Professor of Metallurgical and Materials Engineering, Colorado School of Mines
Primary Researchers: Joghee Prabhuram, Postdoctoral Fellow, Colorado School of Mines
Daniel Clark, Graduate Student, Colorado School of Mines

This project concerns the materials science of Nb/NbO_x bilayers, which we investigated in collaboration with the US Army NSRDEC and MIT Lincoln Laboratory as substrates for MIM (metal-insulator-metal) diodes. In this project, we have developed a versatile method to create high performance Nb/NbO_x bilayers for MIM applications through a highly tunable NbO_x anodization process. Our partners have recently succeeding in integrating these Nb/NbO_x bilayer substrates into MIM antenna array diodes (see **Figure 1**). Our Nb-based MIM technology is particularly well suited for this application because it is capable of a more broadband absorption than metals with stronger plasmonic effects such as Al (albeit at the cost of a weaker resonance). **Figure 2** contrasts simulated absorption spectra from an Al-Al2O3-Al ("AoA") microrectenna array vs. absorption spectra from an Nb-NbOx-Au ("GoN") microrectenna array. The broadband absorption produced by Nb-NbOx-Au rectenna highlights the suitability of this materials system for the rectenna-diode application.

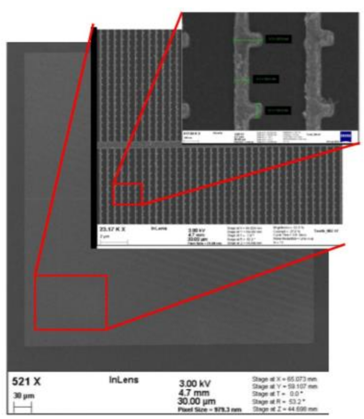

Figure 1. MIM diode rectennea arrays developed by our colleagues at NSRDEC using our Nb/NbOx bilayer substrates. Successive magnifications reveal good large-area uniformity

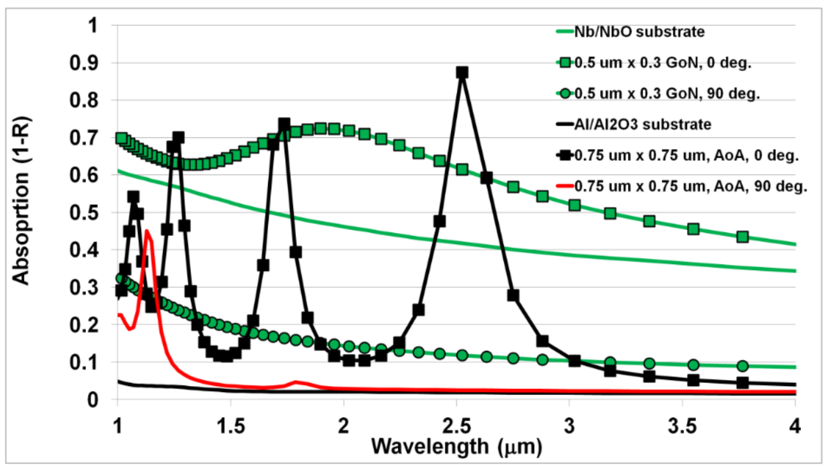

Figure 2. Simulated absorption spectra from an Al/Al2O3 substrate and a Al-Al2O3-Al ("AoA") microrectenna array vs. absorption spectra from an Nb/NbOx substrate and an Nb-NbOx-Au ("GoN") microrectenna array. The broadband absorption provided by our Nb-NbOx-Au ("GoN") microrectenna array confirms the excellent suitability of this materials system for the MIM rectenna diode application.

Because reproducibility is key for the long-term application of these MIM systems, our project focused on the following key issues:

1) **Demonstrate reproducible thickness tuning of the NbO_x layer from 10-20nm with +/-2 nm thickness control.**

Our electrochemical anodization technique enables highly reproducible NbO_x oxide thickness control. We have quantified how the oxide growth depends on the anodization voltage and the anodization time. However, we have recently determined that the NbOx growth rate also depends on the thickness of the Nb base metal layer. We hypothesize that the Nb layer thickness affects the electric field established across the Nb/NbOx bilayer film, and thus alters the NbOx anodization rate. We have recently quantified this effect by showing that anodization time increases by approximately a factor of 10 when the Nb metal film thickness is doubled from ~60nm to ~120nm. Our quantification of this sub-linear effect has allowed us to establish reproducible thickness tuning of the NbOx layer for different values of the desired Nb base layer thickness.

2) **Achieve uniform oxide layer smoothness and thickness across macro-scale substrates.**

In order to obtain large-area patterned MIM diode arrays which could be used for microrectenna arrays of interest to the US Army and DoD for military applications like detection of signals and/or power harvesting in the infrared (and possibly the visible) regime, the thickness of the NbOx oxide layer must not change significantly (no more than +/- 2nm). Furthermore, this thickness must remain within tolerance over large macroscopic distances (e.g. over mm or even cm-scale distances) across sample substrates. As shown in Table I, which provides oxide thickness results extracted from a series of TEM cross-sections taken over cm-scale distances across a single sample, careful optimization of the anodization process enables this thickness control to be achieved with +/- 2nm variation.

Table I. NbOx thickness variation versus location for one macroscopic MIM sample.

TEM CROSS-SECTION LOCATION ON SAMPLE	MEASURED NIOBIUM OXIDE THICKNESS
EDGE OF SAMPLE	19.4 nm
1 CM FROM EDGE	19.5 nm
MIDDLE OF SAMPLE (~2CM FROM EDGE)	18.7 nm

A full summary of the TEM analysis we conducted on these Nb/NbOx samples in support of our US Army NSDREC collaborators in provided in Figures 3-10 and Table II below. The Scanning/transmission electron microscope (S/TEM) micrographs were collected on an FEI Talos F200X 200 keV field emission S/TEM equipped with an FEI X-FEG high brightness Schottky FEG and the SuperX energy-dispersive x-ray spectroscopy (EDS) system which includes four SDD detectors EDS symmetrically placed around the sample and a 16MP CMOS camera, the FEI Ceta 16M camera. EDS maps were collected with a dwell time of 3 µs of SiKα, NbKα, PtKα, and OKα, and were analyzed using Bruker ESPIRT software. A working distance of 60 mm for the bright-field (BF) and high angle annular dark field (HAADF) S/TEM micrographs. All micrographs were collected oriented down the 110 axis of the Si substrate.

Table II. Summary of Nb/NbOx bilayer samples studied in this project. For each sample, thickness was measured in 5 different areas on the HAADF micrograph using Image J.

Batch	Sample	Nb thickness (nm)	St. Dev (nm)	Nb2O5 thicknes (nm)	St. Dev. (nm)	Total Thickness (nm)	Resistance (ohmcm)
I	5	109.5	0.7	23.7	0.9	133.2	79.4
I	6	102	1.2	24.6	0.4	126.6	54.7
I	8	109.3	0.8	23.7	0.2	133.0	63.6
I	9	82.8	2.5	16.2	1.2	99.0	65.7
I	11	103	1.7	24.5	0.5	127.5	83.5
II	3	99.8	1.4	24.7	1	124.5	80.9
II	4	103	0.5	14.2	0.7	117.2	72.7
II	5	91.3	0.6	20.7	1	112.0	62.3

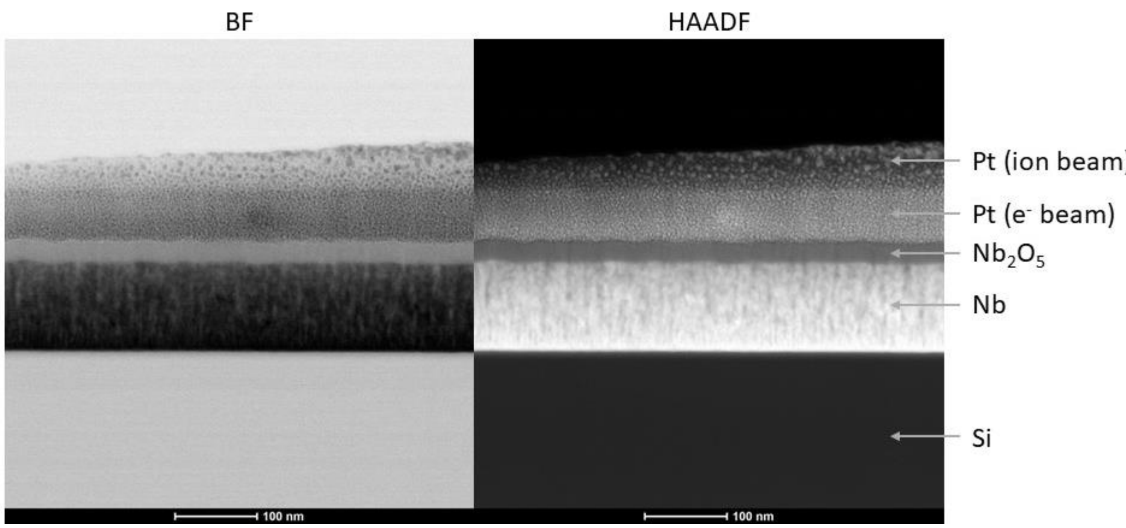

Figure 3. Representative cross-sectional image of a Nb/NbOx bilayer with individual layers identified. The Pt capping layer is applied for FIB processing.

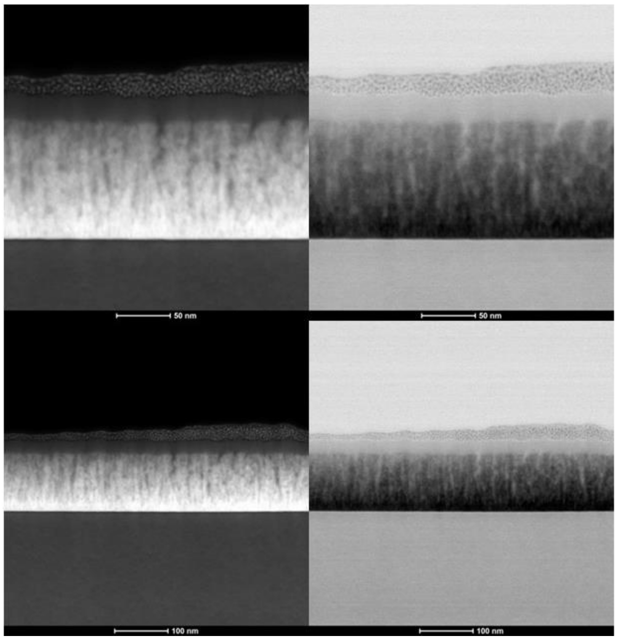

Figure 4. Representative cross-sectional images of Sample 5, batch I.

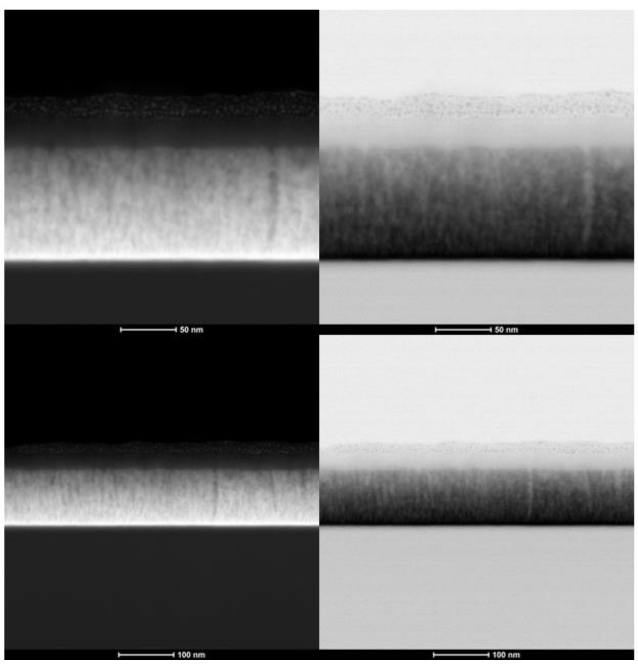

Figure 5. Representative cross-sectional images of Sample 6, batch I.

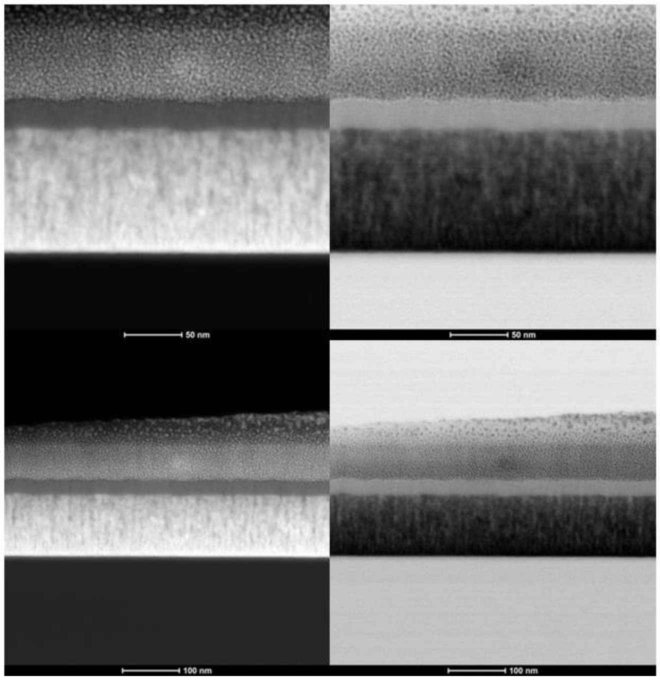

Figure 6. Representative cross-sectional images of Sample 8, batch I.

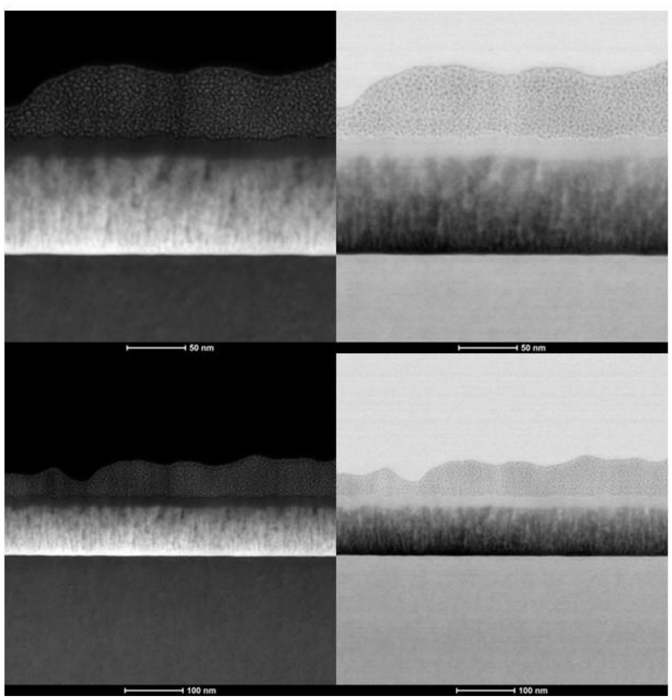

Figure 7. Representative cross-sectional images of Sample 9, batch I.

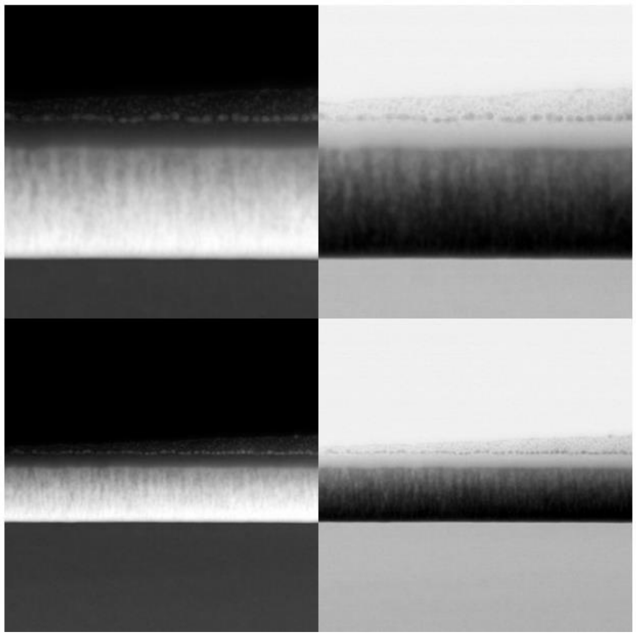

Figure 8. Representative cross-sectional images of Sample 3, batch II.

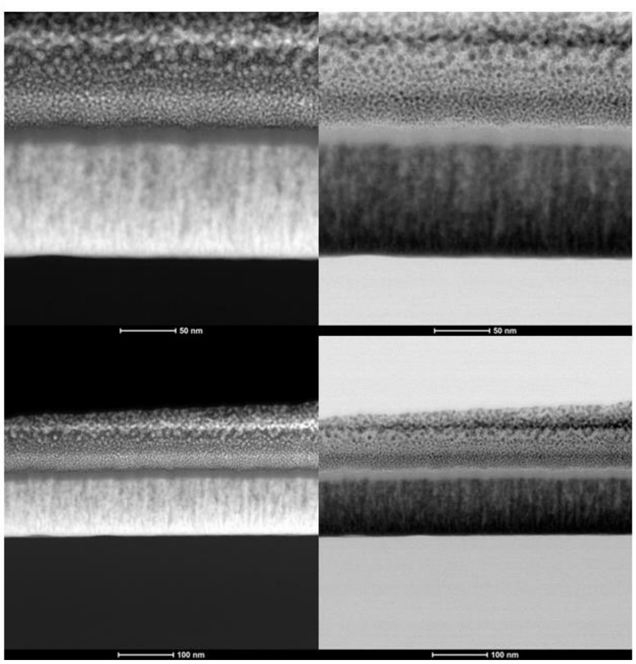

Figure 9. Representative cross-sectional images of Sample 4, batch II.

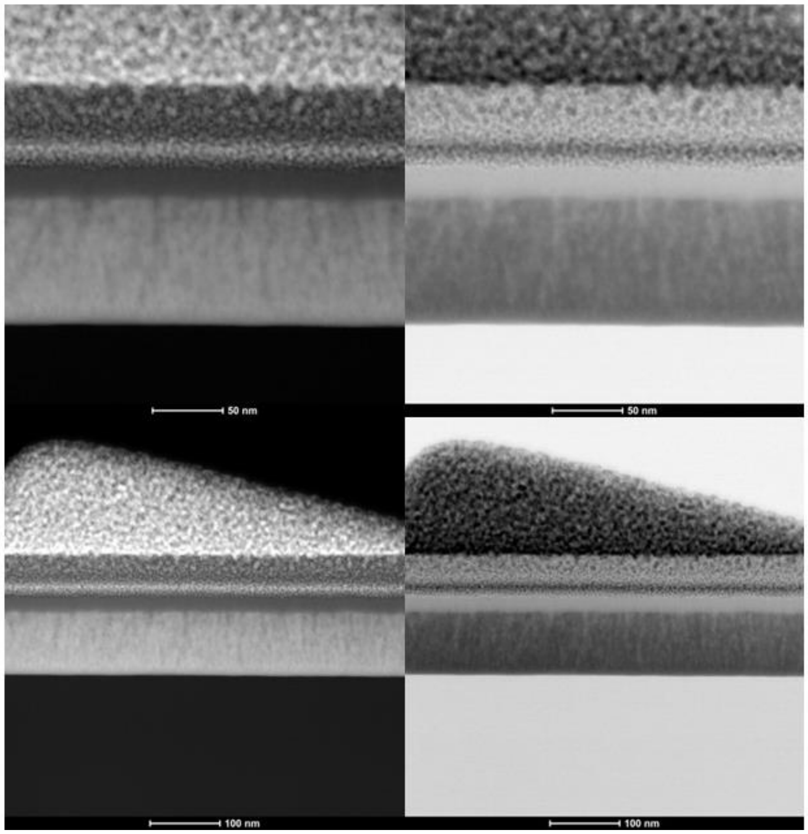

Figure 10. Representative cross-sectional images of Sample 5, batch II.