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# Synthesis and Accelerated Testing of Oxynitride Films for High Temperature Applications

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## Preview of Award 0840045 - Final Project Report

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### Cover

Federal Agency and Organization Element to Which Report is Submitted:	4900
Federal Grant or Other Identifying Number Assigned by Agency:	0840045
Project Title:	Synthesis and Accelerated Testing of Oxynitride Films for High Temperature Applications
PD/PI Name:	Robert J Lad, Principal Investigator Rosemary L Smith, Co-Principal Investigator
Recipient Organization:	University of Maine
Project/Grant Period:	09/15/2008 - 08/31/2013
Reporting Period:	09/01/2012 - 08/31/2013
Submitting Official (if other than PD\PI):	Robert J Lad Principal Investigator
Submission Date:	02/09/2014
Signature of Submitting Official (signature shall be submitted in accordance with agency specific instructions)	Robert J Lad

### Accomplishments

#### \* What are the major goals of the project?

**This project focused on the development of next generation oxynitride ceramic thin film coatings that can potentially withstand harsh environments with service temperatures >1000-1500oC for use in applications such**

as high temperature sensors, turbine engine components, aerospace propulsion systems, cutting tools, and other high temperature structural materials. Oxynitride thin film materials based on the Si-Al-O-N and Si-Zr-O-N systems were synthesized using reactive magnetron co-sputtering. Analysis of the stoichiometry, structure, and morphology of oxynitride films with different architectures was correlated with high temperature oxidation, thermal shock, morphology changes, and nanomechanical properties. SiAlON and SiZrON films were coated on various substrate materials and their oxidation resistance, hardness, and wear resistance were evaluated in both laboratory and industry R&D test environments. SiAlON films remain amorphous even when heated up to 1500oC and they have excellent wear resistance. SiZrON films are either amorphous or contain nano-sized ZrO<sub>2</sub> or ZrN precipitates depending on the exact film composition. Both types of films have high hardness and act as good oxidation barriers.

**\* What was accomplished under these goals (you must provide information for at least one of the 4 categories below)?**

Major Activities:

*Preparation and submission of three peer-reviewed publications that report research results:*

- Paper published: "Properties of SiAlO<sub>2</sub>N Protective Coatings on Surface Acoustic Wave Devices" *Thin Solid Films*
- Paper submitted: "Properties of Amorphous SiAlON Thin Films Grown by RF Magnetron Co-Sputtering" *Surface & Coatings Technology*
- Paper submitted: "Nanostructure, Bonding, and High Temperature Oxidation of Si-Zr-O-N Thin Films" *Thin Solid Films*

*Training and mentoring of undergraduate students:*

- Julia Sell – Undergraduate Physics major (junior); Project: Investigation of Au-doped SiAlON films; REU student during Summer – Fall 2013.
- Sean Seekins – Undergraduate Chemical Engineering major (senior); Project: Characterization of SiZrON thin films; undergraduate research during Fall 2012 – Spring 2013.

*Technology transfer to industrial collaborators:*

- Environetix Technologies Corp. (Orono, ME) - Prototype protective SiAlON coatings on harsh environment wireless high temperature sensor devices.
- New Concepts Engineering (Windham, ME) – Prototype wear-resistant SiAlON coatings on metallized plastic bottles.
- The Hope Group (South Portland, ME) – Prototype wear-resistant SiAlON coatings on piston shoes within the hydraulic transmission of a biofuel-powered diesel locomotive engine for the Mt. Washington Cog Railway.
- Directed Vapor Technologies International, Inc. (Charlottesville, VA) – Collaborated on Army SBIR Phase I proposal submitted by DVTI to investigate high rate e-beam evaporation of Si-Al-O-N and Si-Zr-O-N coatings on aircraft gear steels.

Specific Objectives:

For this most recently completed no-cost extension period, the objective was to complete experimental work and submit manuscripts that report results on both SiAlON and SiZrON thin film systems. The no-cost extension was necessary since a PhD graduate student working on the project since 2009 had to withdraw from the program due a medical condition. Undergraduate students were hired during the past year to continue the work.

Significant Results:

(1) A paper entitled "Properties of SiAlO<sub>2</sub>N Protective Coatings on Surface Acoustic Wave Devices" was published in *Thin Solid Films* 534 (2013) 198-204

ABSTRACT: The use of a protective wear-resistant amorphous SiAlO<sub>2</sub>N thin film overlayer (amorphous SiO<sub>2</sub>-AlN alloy) on top of surface acoustic wave (SAW)

devices is demonstrated on both quartz and langatate substrates. SiAlO<sub>2</sub>N films were deposited by RF magnetron sputtering onto sapphire substrates, quartz SAW devices, and langatate SAW devices. The SiAlO<sub>2</sub>N layer had an amorphous structure, a density of  $2.8 \pm 0.1$  g/cm<sup>3</sup>, a roughness less than 1 nm as measured by X-ray reflectivity, and a dielectric permittivity of  $7.5 \pm 0.05$  as determined from microfabricated SiAlO<sub>2</sub>N capacitors. SiAlO<sub>2</sub>N elastic constants C<sub>11</sub> and C<sub>44</sub> were extracted using a numerical implementation of the matrix method for SAWs traveling in multilayer structures, and were found to be  $C_{11} = 160 \pm 30$  GPa and  $C_{44} = 55 \pm 5$  GPa. The operating frequencies and transmission losses of quartz SAW devices covered with SiAlO<sub>2</sub>N coatings were only slightly perturbed, but the temperature coefficient of delay (TCD) near 100°C increased significantly by 250 ppm/oC. For langatate SAW devices, the SiAlO<sub>2</sub>N coating contributed an additional 8.5 dB loss but the TCDs were minimally affected for SiAlO<sub>2</sub>N thicknesses up to 800 nm. This result suggests that langatate SAW devices requiring temperature compensation can be designed without consideration of the multi-layer structure, which greatly simplifies device design and modeling.

(2) A paper entitled "Properties of Amorphous SiAlON Thin Films Grown by RF Magnetron Co-Sputtering" was submitted to *Surface & Coatings Technology*.

ABSTRACT: SiAlON thin films were deposited by RF magnetron co-sputtering of Al and Si targets in Ar/O<sub>2</sub>/N<sub>2</sub> mixtures to a thickness of ~200 nm onto both bare and Pt-coated r-cut sapphire substrates. Films deposited at 200°C are amorphous as determined from X-ray diffraction (XRD) and have < 1 nm RMS roughness as measured by X-ray reflectivity (XRR). *In situ* X-ray photoelectron spectroscopy (XPS) measurements from films grown over a wide range of Si<sub>x</sub>Al<sub>y</sub>O<sub>z</sub>N<sub>100-x-y-z</sub> stoichiometries indicate that a homogenous amorphous phase is formed over all compositional regions of the quaternary thin film phase diagram. After annealing at 1000°C for 10 hours in vacuum, the film stoichiometries remained nearly unchanged and the films retained an amorphous structure, as verified by XRD. The films lost nitrogen during air exposure at 1000°C, leading to the formation of an amorphous aluminum silicate layer at the surface. No crystalline SiAlON phases, which have been reported for bulk SiAlON materials, were observed in films even after heating at 1500°C for 10 days. Pin-on-disk measurements showed that SiAlON films have negligible wear up to 80 gram loads, while significant wear occurs on the sapphire pin in sliding contact, indicating that the SiAlON films have excellent wear resistance.

(3) A paper entitled "Nanostructure, Bonding, and High Temperature Oxidation of Si-Zr-O-N Thin Films" was submitted to *Thin Solid Films*.

ABSTRACT: A series of Si-Zr-O-N thin films were grown on r-sapphire substrates using RF magnetron co-sputtering of Zr and Si targets in Ar-O<sub>2</sub>-N<sub>2</sub> gas mixtures. X-ray photoelectron spectroscopy shows evidence for different chemical states of nitrogen as bonding in the films changes from covalent to ionic nature with increasing Si-O content. As-deposited films grown at 200°C are amorphous over the entire Si-Zr-O-N compositional range. Heating to 1000°C in air leads to loss of nitrogen in the surface region and precipitation of tetragonal-ZrO<sub>2</sub> nanocrystals in an amorphous film matrix. When the Si-Zr-O-N composition is oxygen-rich, the orientation of the t-ZrO<sub>2</sub> nanocrystals is nearly random within the amorphous film, but for nitrogen-rich films on r-sapphire substrates, the t-ZrO<sub>2</sub> nanocrystals are highly textured with (101) heteroepitaxial orientation induced by reaction with oxygen from the sapphire substrate and t-ZrO<sub>2</sub> nucleation at the sapphire/film interface.

(4) Julia Sell, an undergraduate physics major from Cushing, ME, participated in UMaine's *Summer 2013 REU Program "Sensor Science & Engineering."* In her REU project, Julia used x-ray photoelectron spectroscopy and uv-vis optical spectroscopy to characterize gold-doped SiAlON thin films. The goal of her project was to determine whether the optical band gap of SiAlON thin films could be modified via gold doping. Her results showed that the SiAlON band gap can be modified at small gold dopant concentrations, but gold precipitates are formed in the amorphous SiAlON matrix at dopant levels > 0.5 at% Au, which prevents further changes to the band gap. The preliminary results from her REU project have formed the basis of a collaboration with Chris Applett at Sandia National Lab, and a proposal submitted for FY14 Sandia internal research funds (LDRD) to explore amorphous SiAlON materials as nuclear radiation adsorber layers in radiovoltaic power sources.

Key outcomes or  
Other achievements:

After having obtained promising results concerning wear-resistance and high temperature corrosion-resistance of SiAlON films in the laboratory, collaborations were developed with several companies in the State of Maine to evaluate the performance of SiAlON coatings on different industrial components in a real world environment. During the past year, industrial collaborators have included:

Environetix Technologies Corp. (Orono, ME) - Environetix is a start-up company that is developing and commercializing harsh environment wireless high temperature sensors based on microwave acoustic technology. Prototype protective SiAlON coatings have been attached to rotating parts at the exhaust of a small-scale 'JetCat' turbine engine, and they have yielded improved device stability compared to bare sensor devices.

New Concepts Engineering (Windham, ME) – Prototype wear-resistant SiAlON coatings have been deposited onto metallized plastic bottles. These metallized parts typically contain a UV-curable coating to protect the metal layer from scratching, corrosion, or other damage. SiAlON films are being evaluated as an alternative wear-resistant layer since they potentially can be deposited in the same vacuum chamber as the metallization and provide improved scratch resistance.

The Hope Group (South Portland, ME) – The Hope Group specializes in motion and control systems, including hydraulics, pneumatics, and electrical & electronic control. They have been contracted by the New Hampshire Mt. Washington Cog Railway to solve a cavitation erosion problem with piston shoes operating within the hydraulic transmission of their new biofuel-powered diesel locomotive engine. Prototype SiAlON coatings are being evaluated on eight separate piston shoes to determine if they can inhibit the cavitation wear process.

Directed Vapor Technologies International Inc. (Charlottesville, VA) - Collaboration has been established with DVTI which has led to the submission of an Army SBIR Phase I proposal to investigate the feasibility of high rate deposition of SiAlON and SiZrON films as hard wear resistant coatings on aircraft gear steels. UMaine will aid in pin-on-disk wear tests and microstructural characterization of prototype films.

**\* What opportunities for training and professional development has the project provided?**

This project enabled undergraduate physics student, Julia Sell, to have her first research experience as a participant in UMaine's NSF-REU "Sensor Science & Engineering" program ([web.eece.maine.edu/research/URP/](http://web.eece.maine.edu/research/URP/)). She completed a course in "Introduction to Sensors" and carried out research using specialized sensor science and engineering research facilities within the UMaine's Laboratory for Surface Science & Technology ([www.umaine.edu/lasst/](http://www.umaine.edu/lasst/)). In particular, she received hands-on training on equipment for RF magnetron sputter deposition of films, X-ray photoelectron

spectroscopy (XPS), X-ray diffraction (XRD), and uv-vis optical absorption spectroscopy. She received an award for best oral presentation at UMaine's 2013 REU Sensors Conference.

Undergraduate chemical engineering student, Sean Seekins, received training on X-ray diffraction (XRD) including grazing incidence diffraction and pole figures, and X-ray photoelectron spectroscopy (XPS) including Ar+ ion depth profiling. Dr. George Bernhardt, a LASST Research Scientist, aided in the training.

#### \* How have the results been disseminated to communities of interest?

Project highlights were communicated to a variety of audiences including students from the Girls Engineer Maine program; 4-H groups; high school students from Central High School in Corinth, ME; undergraduates participating in the REU program; and several Maine legislators.

General aspects of the program were also included in a MRS video about UMaine's Laboratory for Surface Science & Technology (LASST) highlighted at the Fall 2012 MRS Meeting in Boston, MA. The video is available on the following website: <http://www.youtube.com/watch?v=1l6qkkm5lpM>

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## Products

### Books

### Book Chapters

### Conference Papers and Presentations

### Inventions

Nothing to report.

### Journals

Bernhardt, G.P., Krassikoff, J.I., Sturtevant, B.T., Lad, R.J. (). Properties of Amorphous SiAlON Thin Films Grown by RF Magnetron Co-Sputtering. *Surface & Coatings Technology*. . Status = SUBMITTED; Acknowledgment of Federal Support = Yes ; Peer Reviewed = Yes

Byrne, M.S., Seekins, S.A., Bernhardt, G.P., Lad, R.J. (). Nanostructure, Bonding, and High Temperature Oxidation of SiZrON Thin Films. *Thin Solid Films*. . Status = SUBMITTED; Acknowledgment of Federal Support = Yes ; Peer Reviewed = Yes

Sturtevant, B.T., Pereira da Cunha, M., Lad, R.J. (2013). Properties of SiAlO<sub>2</sub>N Protective Coatings on Surface Acoustic Wave Devices. *Thin Solid Films*. 534 198. Status = PUBLISHED; Acknowledgment of Federal Support = Yes ; Peer Reviewed = Yes

### Licenses

Nothing to report.

### Other Products

Nothing to report.

### Other Publications

### Patents

Nothing to report.

### Technologies or Techniques

Nothing to report.

## Thesis/Dissertations

### Websites

Nothing to report.

## Participants/Organizations

### What individuals have worked on the project?

Name	Most Senior Project Role	Nearest Person Month Worked
Lad, Robert	PD/PI	2
Smith, Rosemary	Co PD/PI	0
Bernhardt, George	Staff Scientist (doctoral level)	1
Seekins, Sean	Undergraduate Student	2
Sell, Julia	Research Experience for Undergraduates (REU) Participant	3

### Full details of individuals who have worked on the project:

#### Robert J Lad

**Email:** rjlad@maine.edu

**Most Senior Project Role:** PD/PI

**Nearest Person Month Worked:** 2

**Contribution to the Project:** Overall project director; responsible for advising undergraduate students - planning experiments and analyzing data.

**Funding Support:** None

**International Collaboration:** No

**International Travel:** No

#### Rosemary L Smith

**Email:** rosemary.smith@maine.edu

**Most Senior Project Role:** Co PD/PI

**Nearest Person Month Worked:** 0

**Contribution to the Project:** Member of student thesis committees; advise students on data interpretation

**Funding Support:** None

**International Collaboration:** No

**International Travel:** No

#### George Bernhardt

**Email:** George\_Bernhardt@umit.maine.edu  
**Most Senior Project Role:** Staff Scientist (doctoral level)  
**Nearest Person Month Worked:** 1

**Contribution to the Project:** Trained students on thin film deposition, XPS, and XRD.

**Funding Support:** None

**International Collaboration:** No  
**International Travel:** No

**Sean Seekins**

**Email:** Sean\_Seekins@umit.maine.edu  
**Most Senior Project Role:** Undergraduate Student  
**Nearest Person Month Worked:** 2

**Contribution to the Project:** Performed research on characterization of SiZrON thin films using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) depth profiling.

**Funding Support:** None

**International Collaboration:** No  
**International Travel:** No

**Julia Sell**

**Email:** julia.sell@maine.edu  
**Most Senior Project Role:** Research Experience for Undergraduates (REU) Participant  
**Nearest Person Month Worked:** 3

**Contribution to the Project:** Undergraduate participant in REU program; carried out research using specialized sensor science and engineering research facilities within the UMaine's Laboratory for Surface Science & Technology. In particular, she deposited thin films by RF magnetron sputter deposition, and analyzed them using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and uv-vis optical absorption spectroscopy.

**Funding Support:** None

**International Collaboration:** No  
**International Travel:** No  
**Year of schooling completed:** Junior  
**Home Institution:** University of Maine  
**Government fiscal year(s) was this REU participant supported:** 2013

**What other organizations have been involved as partners?**

Name	Type of Partner Organization	Location
Directed Vapor Technologies International Inc.	Industrial or Commercial Firms	Charlottesville, VA
Environetix Technologies Corporation	Industrial or Commercial Firms	Orono, ME
New Concepts Engineering, LLC	Industrial or Commercial Firms	Winham, ME



**Full details of organizations that have been involved as partners:**

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**Directed Vapor Technologies International Inc.****Organization Type:** Industrial or Commercial Firms**Organization Location:** Charlottesville, VA**Partner's Contribution to the Project:**

Collaborative Research

**More Detail on Partner and Contribution:** Collaboration on feasibility of using SiAlON or SiZrON coatings on aircraft gear steel for Army SBIR Phase I proposal

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**Environetix Technologies Corporation****Organization Type:** Industrial or Commercial Firms**Organization Location:** Orono, ME**Partner's Contribution to the Project:**

Collaborative Research

**More Detail on Partner and Contribution:** Testing of prototype SiAlON films on harsh environment wireless sensor devices

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**New Concepts Engineering, LLC****Organization Type:** Industrial or Commercial Firms**Organization Location:** Winham, ME**Partner's Contribution to the Project:**

Collaborative Research

**More Detail on Partner and Contribution:** Testing of prototype wear-resistant SiAlON coatings on metallized plastic bottles.

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**The Hope Group****Organization Type:** Industrial or Commercial Firms**Organization Location:** South Portland, ME**Partner's Contribution to the Project:**

Collaborative Research

**More Detail on Partner and Contribution:** Incorporation of prototype wear-resistant SiAlON coatings on piston shoes within the hydraulic transmission of a biofuel-powered diesel engine

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**What other collaborators or contacts have been involved?**

NO

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## Impacts

### **What is the impact on the development of the principal discipline(s) of the project?**

The development of corrosion-resistant and wear-resistant SiAlON and SiZrON oxynitride thin film coatings that can withstand harsh environments above 1000oC has important ramifications for a range of technologies including high temperature sensors, turbine engines, ceramic manufacturing, and structural materials used in aeronautic, aerospace, and power generation applications. Experiments have been carried out to test and evaluate the oxidation resistance and mechanical properties of this new class of high temperature ceramic oxynitride coatings with nano-structured architectures. In addition to publication in scientific journals, the results of SiAlON and SiZrON film synthesis and characterization have been transitioned to the industrial sector via testing of prototype coatings on engineering components for several industrial collaborators.

### **What is the impact on other disciplines?**

Both SiAlON and SiZrON films are potentially useful as wear-resistant protective coatings at lower temperatures, including room temperature. The films could impact a diverse number of engineering applications including microelectronic devices, high volume packaging products, seals and bearings, and radiovoltaic power sources, just to name a few.

### **What is the impact on the development of human resources?**

During the past year, this project has supported the training and professional development of two undergraduate students. Julia Sell, a junior physics major at UMaine, received her first laboratory research experience, and was trained on several state-of-the-art materials synthesis and characterization tools. Sean Seekins, a senior chemical engineering major at UMaine, carried out materials characterization research which helped formulate his career plans, and is currently applying to several materials science & engineering graduate programs.

### **What is the impact on physical resources that form infrastructure?**

The research was carried out within the Thin Film Synthesis and Processing Facility in the Laboratory for Surface Science & Technology (LASST) at UMaine. The thin film deposition and materials characterization instrumentation in this facility are a major component of LASST and are used for many federally funded projects and industry collaborations.

### **What is the impact on institutional resources that form infrastructure?**

Nothing to report.

### **What is the impact on information resources that form infrastructure?**

Nothing to report.

### **What is the impact on technology transfer?**

Prototype oxynitride films were deposited on engineering parts for several industry collaborators and tested in the field. Examples include protective coatings on wireless harsh environment sensors (Environetix Technologies Corp.), wear-resistant coatings on metallized plastic bottles (New Concept Engineering, LLC), and wear-resistant coatings on piston shoes in biofuel diesel engines (The Hope Group).

### **What is the impact on society beyond science and technology?**

The use of oxynitride coatings will extend the lifetime of components used in high temperature harsh environments, leading to lower materials costs and energy savings through more efficient high temperature processes.

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## Changes/Problems

### **Changes in approach and reason for change**

Nothing to report.

### **Actual or Anticipated problems or delays and actions or plans to resolve them**

Nothing to report.

### **Changes that have a significant impact on expenditures**

Nothing to report.

### **Significant changes in use or care of human subjects**

Nothing to report.

### **Significant changes in use or care of vertebrate animals**

Nothing to report.

### **Significant changes in use or care of biohazards**

Nothing to report.