Submitted on:  08/14/2003  
Principal Investigator: Camata, Renato P.  
Award ID:  0116098  
Organization: U of Alabama Birmingham  
Title:  Development of a Multi-Purpose Laser Deposition Facility for Research and Education in Nanostructured Materials

**Project Participants**

**Senior Personnel**

Name: Camata, Renato  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Lacefield, W.  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Vohra, Yogesh  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Lawson, Christopher  
Worked for more than 160 Hours: No  
Contribution to Project:  

Name: Mirov, Sergey  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Scholz, Carmen  
Worked for more than 160 Hours: No  
Contribution to Project:  

Name: Gerakines, Perry  
Worked for more than 160 Hours: No  
Contribution to Project:  

**Post-doc**

**Graduate Student**

Name: Bulut, Mevlut  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Kim, Hyunbin  
Worked for more than 160 Hours: Yes  
Contribution to Project:  

Name: Sweitzer, Robyn
Worked for more than 160 Hours: No
Contribution to Project:

Name: Wang, Shengyuan

Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Matsumura, Masashi

Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Cunningham, Nicholas

Worked for more than 160 Hours: No
Contribution to Project:

Undergraduate Student

Name: Bray, Jennifer

Worked for more than 160 Hours: No
Contribution to Project:

Name: Cox, Stan

Worked for more than 160 Hours: No
Contribution to Project:

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Name: Kirchhoff, Jennifer

Worked for more than 160 Hours: No
Contribution to Project:

- Years of schooling completed: Sophomore
- Home Institution: Other than Research Site
- Home Institution if Other: Carnegie Mellon University
- Home Institution Highest Degree Granted (in fields supported by NSF): Doctoral Degree
- Fiscal year(s) REU Participant supported: 2002
- REU Funding: No Info

Name: Richardson, Andreece

Worked for more than 160 Hours: No
Contribution to Project:

- Years of schooling completed: Junior
- Home Institution: Other than Research Site
- Home Institution if Other: Alcorn State University, Mississippi
- Home Institution Highest Degree Granted (in fields supported by NSF): Master's Degree
Fiscal year(s) REU Participant supported: 2002
REU Funding: No Info
Name: Davis, Gregory
Worked for more than 160 Hours: No
Contribution to Project:

- Years of schooling completed: Sophomore
- Home Institution: Other than Research Site
- Home Institution if Other: Miles College, Birmingham, AL
- Home Institution Highest Degree Granted (in fields supported by NSF): Bachelor's Degree

Fiscal year(s) REU Participant supported: 2003
REU Funding: No Info
Name: Plumlee, Chris
Worked for more than 160 Hours: No
Contribution to Project:

- Years of schooling completed: Junior
- Home Institution: Other than Research Site
- Home Institution if Other: Arizona State University
- Home Institution Highest Degree Granted (in fields supported by NSF): Doctoral Degree

Organizational Partners

University of Alabama in Huntsville
George C. Marshall Space Flight Center

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings:
Demonstration of deposition of textured (i.e., preferentially oriented) hydroxyapatite coatings with distinct mechanical properties as compared to random films.


Demonstration that thin calcium phosphate coatings produced by pulsed laser deposition have sufficient bond strength (> 50 Mpa) sufficient resistance to dissolution, to indicate their successful use on dental implants.

Successful deposition of ZnS thin films doped with chromium for mid-IR laser applications.

Demonstration of the feasibility of Nanoparticle Beam Pulsed Laser Deposition
Successful deposition of metal nanoparticle/amorphous matrix monolayer composites by Nanoparticle Beam Pulsed Laser Deposition.

Further details on finding available in research and education activities file.

**Training and Development:**
In just 14 months of operation, which began in summer 2002, training and professional development was provided for 15 students and teacher. Out of these 15 individuals involved in projects using the facility funded by this MRI award, 6 of them were women and underrepresented minorities (i.e., 40%). An analysis by trainee categories shows that women and underrepresented minorities accounted for 33% of graduate students (2 out of 6), 57% of undergraduate students (4 out of 7), 50% of high school students (1 out of 2), and 100% of teachers (1 out of 1).

Detailed descriptions of how this training was provided is given in included in the research and education activities file.

**Outreach Activities:**
Outreach activities have focused on involving undergraduate and high school students in hands-on research.

Details are included in the research and education activities file.

**Journal Publications**

**Books or Other One-time Publications**


M. Matsumura and R. P. Camata, "Pulsed Laser Deposition of ZnO Thin Films and Nanostructures on Flexible Substrates for UV Applications", (2003). Abstract, Published


Bibliography: 2003 Fall Meeting of the Materials Research Society, December 1-5, 2003, Boston, Massachusetts

Bibliography: 2003 Fall Meeting of the Materials Research Society, December 1-5, 2003, Boston, Massachusetts

Bibliography: 2003 Fall Meeting of the Materials Research Society, December 1-5, 2003, Boston, Massachusetts


Bibliography: 81st General Session of the International Association for Dental Research, June 25-28, 2003, Göteborg, Sweden


Bibliography: 2002 Meeting of the American Physical Society (Southeastern Section), October 31 ? November 2, 2002, Auburn, Alabama


Bibliography: 5th Conference on Aerospace Materials, Processes, and Environmental Technology (AMPET), September 16 ? 18, 2002 Von Braun Center, Huntsville, Alabama


**Web/Internet Site**

**Other Specific Products**

**Product Type:** Instruments or equipment developed

**Product Description:**
We have developed a novel physical deposition technique based on the combination of Pulsed Laser Deposition (PLD) and gas-phase processing of nanoparticles. The new process is called "Nanoparticle Beam Pulsed Laser Deposition (NBPLD)" and its associated instrument is referred to as "NBPLD source". This method allows the decoupling of the deposition of nanoparticles and gas phase constituents that are often present simultaneously in laser ablation plumes. These processes are decoupled in our method by operating two independent PLD-based sources, such that one source predominantly generates nanoparticles while the other is configured for the production of a gas-phase dominated plume. Nanoparticles of well-controlled size, structure and chemical composition are deposited using NBPLD while gas-phase species are sequentially or simultaneously deposited by conventional PLD. A single Excimer laser is used to irradiate both the NBPLD and conventional laser ablation targets. We employ a removable mirror (for sequential deposition) or a beam splitter (for simultaneous deposition).

**Sharing Information:**
It is being disseminated through publications and presentations

**Contributions**

**Contributions within Discipline:**
The development of the novel technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) is considered as the main contribution to the field of materials research.

**Contributions to Other Disciplines:**
Early results in the properties of Calcium Phosphate coatings deposited using the facility indicate that these materials may have an important impact in health care as it pertains to dental and orthopedic implants.

Preliminary results on transition-metal doped semiconductor thin films also suggest that these novel laser materials may become important for mid-IR laser applications.

**Contributions to Human Resource Development:**
Training of 6 graduate students in materials research.

Exposing 6 undergraduate students to their initiation to materials research.

Inspiring 2 high school students in experimental research.

Interfacing of 1 high school teacher involved in development of high school class materials to enable dissemination of materials science concepts at the high school level.

**Contributions to Resources for Research and Education:**

**Contributions Beyond Science and Engineering:**
Categories for which nothing is reported:

Any Web/Internet Site
Contributions: To Any Resources for Research and Education
Contributions: To Any Beyond Science and Engineering
RESEARCH AND EDUCATION ACTIVITIES

The instrumentation developed under this MRI grant significantly expanded the infrastructure for materials research and education at the University of Alabama at Birmingham (UAB). The previously existing materials deposition facilities were limited to Microwave Plasma Chemical Vapor Deposition, Thermal Oxide Growth, and Aerosol Synthesis of Nanoparticulates. This MRI grant enabled the establishment of a complete Pulsed Laser Deposition laboratory at UAB under the direction of the PI Renato Camata. This addition associated with the aforementioned and recently acquired deposition facilities, and our broad suite of materials characterization equipment are placing UAB at a position to make sizable contributions to materials research and education. This MRI grant has enabled the initiation of the following specific projects using the new facility:

1. Calcium phosphate bioceramic coatings for biomedical implants
2. Novel applications of tetrahedral amorphous carbon
3. Novel hybrid materials platforms for biosensing
4. Zinc Oxide thin films: Heterojunctions and nanostructures
5. Mid-infrared laser materials based on doped ZnS films
6. Laboratory investigations of realistic astrophysical dust grain analogs (Pilot)

Table I shows a summary of the activities performed to date on the facility funded by this grant. These include students and teachers trained, publications, and presentations. It should be noted that at the writing of this report, the funded facility has been in operation for only 14 months. Operations began in summer 2002. The first users were NSF-funded REU students Jennifer M. Kirchhoff and Andreece Richardson (assisted by PI and graduate students). This fact should be taken into account in interpreting the productivity data presented in Table I (i.e., publications, publications in preparation, and presentations). At the moment numerous results reported in conferences are in the process of being distilled into manuscripts for high quality publications. Subsequent interim reports will be submitted to NSF with updates of publications.

It should also be noted that out of the 15 students and teacher involved in projects using this MRI facility, 6 of them were women and underrepresented minorities (i.e., 40%). An analysis by trainee categories shows that women and underrepresented minorities accounted for 33% of graduate students (2 out of 6), 57% of undergraduate students (4 out of 7), 50% of high school students (1 out of 2), and 100% of teachers (1 out of 1).

In the section that follows, a detailed Description of Research Activities using the funded facility is provided. The basic technical aspects, rationale, and status of current research of the various projects are presented and details are given on personnel involvement, and products generated.
**Table I:** Summary of Research and Education Activities performed using the Laser Deposition Facility Developed under MRI Grant DMR-0116098. Funding period: 09/01/2001 – 08/31/2003; Facility began operations in the summer 2002.

<table>
<thead>
<tr>
<th>Major Projects</th>
<th>Grad. Students</th>
<th>UG Students</th>
<th>HS Students</th>
<th>HS Teachers</th>
<th>Publications</th>
<th>Publications in preparation</th>
<th>Presentations</th>
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<tbody>
<tr>
<td>1. Calcium phosphate bioceramic coatings for biomedical implants</td>
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<td>2. Novel applications of tetrahedral amorphous carbon</td>
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<td>3. Novel hybrid materials platforms for biosensing</td>
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<td>4. Zinc Oxide thin films: Heterojunctions and nanostructures</td>
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<td>5. Mid-infrared laser materials based on doped ZnS films</td>
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<td>6. Laboratory investigations of realistic astrophysical dust grain analogs (Pilot)</td>
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<td>Other minor projects</td>
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<td><strong>1</strong></td>
<td><strong>6</strong></td>
<td><strong>22</strong></td>
</tr>
</tbody>
</table>

A representative sample of the users of the instrumentation made possible by this MRI award. Picture taken in the PI’s laboratory during commissioning of the facility and user training in the summer 2002.
DESCRIPTION OF RESEARCH ACTIVITIES

Research Project 1 - Calcium phosphate bioceramic coatings for biomedical implants

Hydroxyapatite (HA) [Ca_{10}(PO_4)_6(OH)_2] among calcium phosphates is commonly coated onto orthopedic and dental metallic implants to speed up bone formation around devices, allowing earlier stabilization in a patient. Studies in the past decade have indicated that pulsed laser deposition (PLD) may be the most suitable means of placing thin HA coatings on these implants because of its demonstrated control over stoichiometry, crystallinity, and nanostructure. These characteristics determine the mechanical properties of the films that must be optimized to improve the performance of load-bearing implants and other devices that undergo bone insertion. In this project graduate student Hyunbin Kim and undergraduate students Stan Cox (School of Dentistry) and Andreece Richardson (REU 2002) have used the PLD facility developed with funding within this program to produce nanostructured and preferentially oriented HA coatings and evaluated their mechanical properties. Pure, highly crystalline HA coatings on Ti-6Al-4V substrates were obtained using a KrF excimer laser (248nm) with energy density of 4-8 J/cm^2 and deposition temperature in the range of 500–700ºC. Scanning electron and atomic force microscopies reveal that our careful manipulation of energy density and substrate temperature has led to films made up of HA grains in the nanometer scale. Broadening of x-ray diffraction peaks as a function of deposition temperature suggests that it may be possible to control the film nanostructure to a great extent. X-ray diffractions also show that as the laser energy density is increased in the 4-8 J/cm^2 range, the coatings become preferentially oriented along the c-axis perpendicular to
the substrate. Nanoindentation measurements show improved hardness and Young’s modulus in oriented films that can be attributed to the crystallites alignment in the anisotropic hexagonal HA structure caused by the highly energetic plume during deposition. Preferential orientation, nanostructure, and phase make-up all significantly influence the mechanical properties. We are currently performing experiments to elucidate this these structure-property relationships. (Research funded by National Institutes of Health: NIDCR 1R01 DE013952-02 A1)

Publications


Presentations


Research Project 2 - Novel applications of tetrahedral amorphous carbon

Within the context of this research project, we have been exploring two distinct thrusts for new applications exploiting some unique mechanical and chemical properties of tetrahedral amorphous carbon (ta-C).

2.1. Novel carbon-based nanostructured materials for low-weight, high-strength, and high-temperature applications.

The B$_x$C$_y$N$_z$ ternary system is one of the most promising materials systems for the engineering of superhard materials with enhanced thermal and chemical stability for
aerospace and industrial applications. The recent high-pressure synthesis of cubic BC$_2$N with hardness higher than that of single crystal cubic BN, reaffirms the long-standing technological potential of these materials. Building on the expertise in nanocrystalline diamond coatings established in our department using Microwave Plasma Chemical Vapor Deposition, and the body of knowledge of PLD synthesis of tetrahedral amorphous carbon (ta-C), graduate student Mevlut Bulut is exploring the creation of novel B$_x$C$_y$N$_z$ nanocrystal/amorphous carbon matrix composites. Because the mechanical properties of these B$_x$C$_y$N$_z$ nanostructured materials are inextricably tied to their nanoscale interfacial chemistry, our goal is the engineering of chemical states at the nanocrystal/nanocrystal or nanocrystal/matrix interface that may lead to controllable interfacial binding, delivering mechanical properties that could be “tuned” on demand by the processing conditions. We will achieve this by independently tailoring nanocrystal and matrix characteristics to obtain viable interface chemistries for effective mechanical exchange at the nanoscale. These materials with ordered structures and interfaces at the nanometer scale may provide the properties required of protective coatings for aerospace propulsion and other industrial applications. Interactions at this scale produce behavior that cannot be extrapolated from properties at higher length scales, and therefore, extensive experimentation guided by state-of-the-art modeling produced by other groups will be used to achieve our goals. At the time of this writing we have completed a study on the influence of deposition parameters on the mechanical properties of the ta-C films deposited by PLD using the funded laser facility. We are now exploring the incorporation of size-selected nanocrystals of different chemical composition and structure into the ta-C film by the novel technique developed with assistance from this grant (NBPLD: Nanoparticle Beam Pulsed Laser Deposition). Our initial attempts focus on the use of our NBPLD source to generate boron carbide nanocrystals and incorporate them into the ta-C matrix. The successful deposition of boron carbide films (B$_4$C) by PLD has been reported recently, and using our NBPLD source we will attempt to expand this method to the creation of a beam of size-selected boron carbide nanocrystals that can be used to engineer new composites. This approach, combined with careful control of the substrate temperature, may provide a new way of creating B-doped ta-C films with improved thermal stability. (Research funded by NASA: UAH/NASA EPSCoR Core Infrastructure Seed Grant).

2.2. Tetrahedral amorphous carbon as an encapsulation layer for implantable microelectronic devices.

Implantable microelectronic devices capable of neural stimulation present a promising pathway to restore basic neural functions in humans where non-regenerative specialized tissue responsible for signal transduction has been permanently damaged. Device flexibility is essential because gap-free alignment within the host tissue is necessary and bending often occurs during implantation. Although molecular electronic devices are desirable for this application, their realization awaits significant advances in that field. Alternatively, generators of neuro-stimuli are within reach of current integrated circuit technology. Challenging performance and reliability issues arise, however, when these flexible prosthetic devices are implanted into soft tissue and exposed to bodily fluids. Polyimide, the well-established polymeric standard for encapsulation of
microelectronic circuits, is hydrophilic enough to allow significant rates of water and ion penetration, which lead to corrosion and device failure. Tetrahedral amorphous carbon (ta-C) is an attractive candidate for protective encapsulating layers on polyimide-laden devices because of its excellent mechanical properties, chemical inertness, and biocompatibility. In this project graduate students Mevlut Bulut (UAB-Physics) and Robyn Sweitzer (UAH-Chemistry) are exploring this encapsulation approach by creating 100-500-nm-thick ta-C films by pulsed laser deposition on polyimide substrates at room temperature. For this purpose they are using the facility funded by this MRI grant. Pyrolytic graphite targets are ablated using a KrF excimer laser (248 nm) in high vacuum at fluences of 5-15 J/cm². Layers show excellent adhesion to the polyimide substrate and Raman measurements confirmed the tetrahedral-carbon nature of films. Atomic Force Microscopy indicates high-quality, dense, pinhole-free ta-C films at optimized 8 J/cm² laser fluence and 3.6 Angstrons/sec deposition rate. Nanoindentation measurements have yielded hardness of 29 GPa and Young’s Modulus of 250 GPa. We are currently using this approach to coat flexible three-dimensional implant simulants that undergo in vivo biocompatibility studies in another facility. Serious materials issues being addressed involve possible negative effect of intrinsic stress present in ta-C on device performance and the stability of ta-C/polyimide interface. This project involves a collaboration of the PI Renato Camata with Prof. Carmen Scholz (Dept. of Chemistry, University of Alabama in Huntsville).

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Research Project 3 - Novel hybrid materials platforms for biosensing

The presence of metal surfaces 5-20 nm from weak fluorophores (e.g., DNA) can increase light absorption and radiative rate of the molecules by factors which can approach $10^3$. Recent studies show that consistent observation of this phenomenon requires nanoengineered metallic surfaces. Since actual adsorption of the biomolecules onto metal nanostructures quenches fluorescence, careful positioning of molecules at appropriate distances is crucial. To study this fluorescence enhancement as a potential route for biomolecule sensing, graduate student Nicholas Cunningham (currently on leave from UAB), undergraduate student Gregory Davis (REU 2003), and high school teacher Debbie Anderson (RET 2003) have worked in the creation of layers comprising metal nanoparticle ensembles of well-defined size and separation embedded in amorphous Al₂O₃ (alumina). Films were deposited using the novel technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) developed within this MRI project. Contrary to conventional PLD, this approach decouples gas-phase species and nanoparticles that often coexist in ablation plumes so that these constituents are manipulated independently. This is achieved by operating two independent PLD-based sources: One source exclusively generates nanoparticles while the other produces gas-phase dominated plumes. Furthermore, NBPLD allows the delivery of a focused or diffuse beam of size-selected nanoparticles to desired locations on a substrate with sub-50
μm resolution. Different gas-phase species are simultaneously (or sequentially) deposited by PLD. In this project silver nanoparticles were deposited on silicon substrates by ablating a silver target at 760 Torr in the NBPLD source using a KrF excimer laser at 1-3 J/cm² fluences. This is followed by deposition of Al₂O₃ layers by ablation of alumina in vacuum at fluences of 5-15 J/cm². Nanoparticle diameter was tuned for different samples (2-15 nm) while Al₂O₃ thickness was varied from 10 to 200 nm. TEM and AFM on a typical sample yield nanoparticle diameter of (8.0 ± 0.6) nm and Al₂O₃ with thickness of ~20 nm. We are now focusing on measurements of total internal reflection fluorescence of biomolecules dispersed on these nanoengineered substrates using photon-counting fluorescence and picosecond time-correlated single photon spectroscopies. This project is being developed in collaboration with Prof. Thomas Nordlund, a biophysicist at UAB.

Presentations


Research Project 4 - Zinc Oxide thin films: Heterojunctions and nanostructures

This MRI grant has allowed the establishment of a robust research program in synthesis and applications of the semiconductor Zinc Oxide (ZnO). We are currently exploring three areas within this major project.

4.1. ZnO Thin Films and Nanostructures on Flexible Substrates For UV Applications

Zinc Oxide (ZnO) is a promising wide bandgap semiconductor for applications in UV light emitting devices and sensors. Although significant advances in bulk and epitaxial growth, p-type doping, and production of high quality contacts are still needed to enable ZnO as a competitor for large scale UV applications, some of its characteristics suggest it may be a suitable material for integration into flexible electronics platforms. Its compatibility with low temperature deposition, the success of ZnO nanostructure synthesis and its relative ductility in thin film form indicate that ZnO may become an important route to deliver UV functionality in flexible electronic devices. Furthermore,
the outstanding piezoelectric properties and anticipated biocompatibility of ZnO suggest that it may be a useful material for integration into biosensing platforms. In order to assess the potential of ZnO in flexible electronics applications, graduate student Masashi Matsumura has created continuous and nanostructured ZnO films on polymeric substrates for evaluation of structural and optical properties. Specifically, we have used pulsed laser deposition (PLD) to deposit ZnO films with thickness between 100 nm and several microns on polyimide substrates at room temperature. A KrF excimer laser (248 nm) operated at fluences of 1-3 J/cm$^2$ was used and films were deposited under O$_2$ atmosphere at a pressure of $10^{-4}$ Bar and temperatures ranging from room temperature to 300°C. Good flexibility characterizes the obtained layers and x-ray diffraction measurements show that films present all reflections of hexagonal ZnO. Samples deposited above 100°C exhibit good adhesion strength to the polyimide substrates. We are now focusing on probing interface states in ZnO/polymer heterostructures through time-resolved photoluminescence. This is because the devices created in our laboratory involve the deposition of ZnO thin films on polymer substrates leading to the formation of oxide-polymer interfaces. The complex interfacial phenomena expected in these systems are not understood and may be highly deleterious or present serious challenges for device performance. As part of his thesis research, graduate student Masashi Matsumura is using time-resolved photoluminescence measurements to study ZnO/polyimide heterostructures in an attempt to identify luminescence features that can be correlated with interface states in our samples.

4.2. Nanostructured ZnO Films by Nanoparticle Beam Pulsed Laser Deposition

Current ZnO research is mainly focused on optimization of bulk and epitaxial growth, p-type doping, and production of high quality metal contacts. Less emphasis has been given to ZnO nanostructures although these also present potential for important applications particularly in biosensing devices. Moreover, low-dimensional ZnO structures (e.g., nanocrystals, nanowires) are already produced with greater purity and better crystal quality than bulk crystals and epilayers as low defect concentrations are statistically favored in these nanoscale systems. In this study, high school student John Harrison (assisted by graduate student Masashi Matsumura) is using a novel technique developed by the PI under this MRI grant and known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) to deposit ZnO nanoparticle/Al$_2$O$_3$ films on silicon and sapphire at room temperature to 400°C. Contrary to conventional PLD, this approach allows decoupling of deposition of nanoparticles and gas-phase species that often coexist in ablation plumes so that these two processes are manipulated independently. This is achieved by operating two independent PLD-based sources, such that one source exclusively generates nanoparticles while the other employs a gas-phase dominated plume. NBPLD delivers a beam of size-selected nanoparticles of controlled chemical composition while gas-phase species of different materials are simultaneously deposited using an independent laser source. Using this technique, we are creating layers of ZnO nanoparticles of well-defined size dispersed in amorphous Al$_2$O$_3$. ZnO nanoparticles are deposited by ablating a ZnO target at 0.3-0.7 Bar in the NBPLD source using a KrF excimer laser (248 nm) at fluences of 1-5 J/cm$^2$ while deposition of Al$_2$O$_3$ was achieved by ablation of alumina targets at 5-10 J/cm$^2$ in a $10^{-4}$ Bar O$_2$ atmosphere. ZnO
nanoparticle diameter was tuned in the 5-15 nm range for different samples. We are now investigating photoluminescence properties of these films with emphasis on size effects and interface phenomena.

4.3. In-Situ Control of Nanoscale Crystallite Size in ZnO Layers for Light Trapping in Thin Film Solar Cells

Within the context of our ZnO synthesis project, we have also started a study on how to control crystallite size in polycrystalline ZnO films. The motivation of this study is the fact that polycrystalline transparent conducting oxides (TCOs) are often integrated into solar cell structures as light trapping media to enhance device efficiency. Although used extensively, there have been few studies attempting optimization of the film crystallite size to achieve maximum performance for this application. One way of generating TCOs with improved crystallite size control is pulsed laser deposition (PLD). This is in part due to the generation of a broad range of particulates during PLD. Although these particulates are undesirable in many cases, they are particularly suitable for creation of controlled nanoscale crystallite size in TCOs. However, in order to control the incorporation of these particulates into the resulting film it is necessary to understand their dynamic behavior before and after deposition. Few studies have concentrated on this problem. This is partially because there are few techniques capable of performing direct in-situ measurements on gas-suspended nano- and submicron particles during materials fabrication. In this work we are targeting the use of low-pressure differential mobility analysis to perform particle spectrometry in the 1-1000 nm size range and study the gas-phase dynamics of nanoparticles formed during KrF pulsed laser deposition of ZnO films with sub-micron crystallite size. ZnO targets are ablated in inert gas atmosphere with background pressures in the 70-400 Torr range and laser fluences of 1-5 J/cm². In-situ measurements on the gas-suspended nanoparticle population are performed during ZnO deposition as a function of pressure and laser fluence. This study is in its early stages of implementation. Our goal at this stage is to investigate how the size distributions measured in the gas phase correlate with the crystallite size of the resulting film as determined by AFM analysis and other microscopy techniques.

Presentations
Research Project 5 - Mid-infrared laser materials based on doped ZnS films

Wide application of II-VI materials doped with Transition Metal ions (TM:II-VI) as mid-IR laser media requires advances in the technology of their synthesis. All the known growth methods such as melt, vapor growth, or after growth thermo-diffusion doping have problems with the control of dopant concentration. In this project, graduate student Shengyuan Wang (now at the University of Alabama) has demonstrated that pulsed laser deposition (PLD) is a promising “alternative route” for synthesis of mid-IR laser media based on chromium doped ZnS crystalline thin films with a precisely controllable concentration of dopant. In order to obtain these films we have used the UAB laser facility funded by this MRI grant.

Presentations

Research Project 6 (Pilot) - Laboratory investigations of realistic astrophysical dust grain analogs

The nature of dust grains in remote environments is derived by spectroscopic techniques involving the absorption or scattering of light. In order to make conclusions about the physical size or chemical composition of these grains, one must have knowledge in hand about the scattering properties of appropriate materials to which the observations may be compared. This information is usually obtained from samples of bulk materials of appropriate compositions. The drawback in this case is that the interaction of light with bulk materials is not representative of the interactions of light with sub-micron sized particles, such as those found in environments such as the interstellar medium (ISM), interplanetary space, or the upper atmosphere of Earth. The effects of scattering are much stronger when the scatterers are on the same size scale as the incident radiation (“resonant scattering”). Therefore bulk properties must be modified according to the rules of Mie Scattering Theory before they are useful to astronomers. Assumptions about grain sizes and shapes must be made in order to generate such a data set. Clearly, measurements performed on single grains of the appropriate sizes and compositions are required to produce a data set that can be directly compared to spectroscopic observations without artificial modifications.

In this pilot project we have started in collaboration with Prof. Perry Gerakines and researchers at NASA Marshall Space Flight Center (MSFC), using this MRI facility to improve understanding of the composition and physical properties of interstellar, interplanetary, or atmospheric dust grains. This is accomplished by the creation of a unique data set, consisting of the infrared scattering properties of sub-micron sized
laboratory-produced dust grains of known compositions, structures, and sizes (or size ranges). This is a unique program in the sense that we study the properties of individual sub-micron-sized dust grains as opposed to aggregates or materials in bulk form as is more common in the literature. The laser facility implemented at UAB from funds provided by this MRI award has allowed the creation of these dust grains that are being studied by astrophysicists at UAB and MSFC. Undergraduate student Jennifer Bray (assisted by graduate student Mevlut Bulut) was involved in the synthesis of these dust grains. The infrared scattering properties of the individual laboratory-produced grains will be correlated to their physical structure and chemical composition. Comparisons of observed astronomical data to our data set of individual grains of relevant compositions, sizes, and structures will provide an unprecedented ability to deduce the properties of astrophysical dust.

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DESCRIPTION OF EDUCATION ACTIVITIES

The laser deposition facility funded by this MRI award has become the centerpiece of the fabrication process for the thesis research of 6 graduate students. This establishes the impact of this grant on graduate education. In the research activities described previously, explicit mention was made of the graduate students whose education has been impacted by this facility. Aside from this traditional role of research instrumentation in graduate education, this facility has served as an important materials fabrication system for undergraduate students and teacher in our NSF-funded REU/RET program. PI Renato Camata is Co-Principal Investigator in the NSF grant associated with this REU/RET-site and is actively involved in the recruitment, selection, and mentoring of students and teachers in this program. Co-PI Yogesh Vohra is the Director of this REU/RET-site. Since the commissioning of this facility in summer 2002, 4 undergraduate students and 1 high school teacher from our REU/RET site were involved in research using this facility. Two additional undergraduates from outside the REU/RET program and 2 high school students were also involved. Our target group for this REU/RET-site are women and underrepresented minorities. Our recruitment focus is on
Undergraduate student Jennifer Kirchhoff measures the substrate temperature during her experiments using an optical pyrometer.

A description of the undergraduate and high school projects conducted are given in what follows.

**Undergraduate Project 1:**

**Title:** Mechanical Properties of YSZ/Al₂O₃ Nanocomposite Thin Films

**Student:** Jennifer M. Kirchhoff (Carnegie Mellon University)

**Advisor:** Renato P. Camata

Yttria-stabilized zirconia (YSZ) is an important material in many emerging technologies such as solid oxide fuel cells, thermal barrier coatings, and multi-layer superconductor structures. While these applications rely primarily on the electrochemical, thermal, and electronic properties of YSZ, the reliability of actual devices is often limited by the inability of YSZ to withstand high mechanical stresses. Bulk YSZ presents indentation hardness above 10 GPa and Young's modulus ~220 GPa. As most ceramics, it displays low fracture toughness and bending strength. Recent studies have shown that YSZ containing 5-10 vol.% Al₂O₃ microparticles exhibit increased fracture toughness and bending strength with manageable adverse effects in thermal and ionic conductivity. The engineering of YSZ/Al₂O₃ composites at the nanoscale, however, remains largely unexplored. In this study undergraduate student Jennifer Kirchhoff started a project to use pulsed laser deposition (PLD) to create micron-thick YSZ films containing well-dispersed, uniformly-sized Al₂O₃ nanoparticles with controlled concentration. Her strategy was to ablate alternately cubic 8-mol.% YSZ and amorphous Al₂O₃ targets with the focused beam of a KrF excimer laser (248 nm) and synchronous control over background atmosphere and pressure. Laser fluence on targets was varied in the 3-10 J/cm² range and films were deposited on silicon and Ti-6Al-4V substrates in the 500°C-800°C range. By varying the background pressure, she attempted to control the nanoparticle average size in the 5-40 nm range. By changing the number of pulses during each cycle, films were deposited with different nanoparticle concentrations ranging from 10¹⁰ to 10¹² cm⁻² per nanoparticle layer. X-ray diffraction measurements on the films show all reflections of cubic YSZ. Nanoindentation measurements yield values of hardness between 0.5 and 1.0 GPa and elastic modulus between 10 and 29 GPa.

**Undergraduate Project 2:**

**Title:** Hydroxyapatite Coatings by Pulsed Laser Deposition

**Student:** Andreece Richardson (Alcorn State University, Mississippi)

**Advisor:** Renato P. Camata

Hydroxyapatite (HA) is used on dentistry and orthopedic implants. Titanium’s (Ti) good corrosion resistance and reasonable fatigue life makes it a reliable replacement for bone as far as structure support is concerned. Although Ti exhibits acceptable biocompatibility in the human body, its combination with a hydroxyapatite (HA) coating has been found to significantly improve its bioactivity. Common techniques used to produce HA coatings are plasma spraying, electrophoretic deposition, ion-beam sputter coating, and flame spraying. A more recently used technique for depositing thin films is the pulsed laser deposition (PLD). The PLD has various diverse capabilities and is well suited to the deposition of complex materials, which also makes it a good choice of method for HA coating. In this study, undergraduate student Andreece Richardson performed experiments to calibrate the deposition conditions of our newly commissioned PLD system to achieve high quality crystalline HA films. In the experiment HA powder targets were ablated under different temperatures, atmospheres, laser density, flow rate, and heating of mixed argon and water. Different amounts of various calcium phosphate phases were found on the films and correlated with deposition conditions.

**Undergraduate Project 3:**

**Title:** Nanoengineered Metallic Surfaces for Fluorescence-based DNA Sensing Applications

**Student:** Gregory T. Davis (Miles College, (HBUC) Birmingham, Alabama)

**Advisors:** Renato P. Camata, Thomas M. Nordlund

Harnessing the unparalleled specificity of DNA for chip-based, rapid, and accurate detection of biological agents may revolutionize health care, environmental protection, and national security. A major roadblock in achieving this goal has been the weak and broadband fluorescence characteristics of DNA molecules. Recent studies have shown, however, that the presence of metal surfaces 5-20 nm from DNA can increase light absorption and radiative rate of the molecules by factors that can approach $10^3$. Metal surfaces with nanoscale features have shown even greater improvement of radiative processes. This fluorescence enhancement requires well-controlled metallic surfaces carefully engineered at the nanoscale. Since actual adsorption of the biomolecules onto
metal nanoparticles quenches fluorescence, it is essential to carefully position the molecules at appropriate distances from nanoparticles. In order to study this fluorescence enhancement as a route for biomolecule detection, undergraduate student Gregory T. Davis created films comprising size-selected metal nanoparticles embedded in Al₂O₃. Films were deposited using Nanoparticle Beam Pulsed Laser Deposition (NBPLD).

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Undergraduate Project 4:

Title: Bulk ZnS and ZnSe Doped with Chromium as Laser Materials
Student: Chris Plumlee (Arizona State University)
Advisor: Sergey B. Mirov

In this project, REU student Chris Plumlee pursued the diffusion doping of ZnS and ZnSe bulk crystals with chromium in order to evaluate this material for mid-IR laser applications. Wide application of II-VI materials doped with transition metal ions as mid-IR laser media requires advances in the technology of their synthesis. At the undergraduate research level, one promising approach to obtain such materials is thermal diffusion doping. A thin film of chromium was evaporated on ZnS and ZnSe crystals and diffusion experiments were carried in the high vacuum environment on the facility funded by this MRI award. This investigation was accompanied by numerical simulations of dopant diffusion profiles expected during experiments.

Undergraduate Project 5:

Title: Hydroxyapatite Coatings for Improving the Performance of TMJ Implants
Student: Stan Cox (UAB – School of Dentistry)
Advisor: William Lacefield

Undergraduate student Stan Cox used pulsed laser deposition (PLD) to coat temporomandibular joint (TMJ) implants with calcium phosphate (CaP). The purpose of this study was to determine the bond strength and durability of hydroxyapatite (HA) and other calcium phosphate (CaP) coatings on titanium alloy. The PLD conditions were adjusted to create coatings that ranged from highly crystalline HA to amorphous CaP. Coatings (2-3 µm) were deposited onto 10 mm diameter Ti alloy discs using a KrF excimer (248 nm) laser at substrate temperatures of 500-650°C, Ar/H₂O pressures of 200-600 mTorr and target-substrate distances of 4.9-7.5 cm. Phase composition was determined by XRD. An epoxy-coated aluminum stud was bonded to each test specimen and cured at 150°C for 1 hr, then pulled in tension. Several coatings were also subjected to dissolution studies in distilled water and a simulated physiologic solution. Bond strength and dissolution behavior were correlated to deposition conditions.

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and Exposition of the American Association for Dental Research (AADR), March 12 – 15, 2003, San Antonio, Texas.


**Undergraduate Project 6:**

**Title:** Laser Synthesis of Cosmic Dust Analogs  
**Student:** Jennifer Bray (UAB – Physics Major)  
**Advisor:** Perry Gerakines

In this project undergraduate student Jennifer Bray (assisted by graduate student Mevlut Bulut) used our facility to synthesize dust grains of the mineral olivine and other carbonaceous materials. In these experiments we used our laser facility to generate cosmic dust particle analogues. In one example, we have generated a gas-suspended population of silicate particles by ablating an olivine target in inert atmosphere. The dust particles produced were analyzed by transmission electron microscopy (TEM), infrared absorption measurements, and single particle UV scattering. They have also been levitated in an electrodynamic balance system in which their single-particle IR scattering properties can be obtained. The infrared scattering properties of the individual laboratory-produced grains will be correlated to their physical structure and chemical composition. Comparisons of observed astronomical data to our data set of individual grains of relevant compositions, sizes, and structures will provide an unprecedented ability to deduce the properties of astrophysical dust. The goal of this on-going research is to improve understanding of the composition and physical properties of interstellar, interplanetary, or atmospheric dust grains.

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**High School Project:**

**Title:** Nanostructured ZnO Films by Nanoparticle Beam Pulsed Laser Deposition  
**Student:** John M. Harrison (Alabama School of Fine Arts, Birmingham, Alabama)  
**Advisor:** Renato P. Camata

In this project high school student John Harrison has targeted the creation of well-controlled nanostructured thin films comprising ZnO nanocrystals embedded in Al2O3 matrices and the study of their optical properties. For this purpose we have used the technique developed with the support of this MRI award, Nanoparticle Beam Pulsed Laser Deposition (NBPLD), to deposit ZnO nanoparticle/Al2O3 films on silicon and sapphire at temperatures ranging from room temperature to 400ºC. The NBPLD technique enables the variation of nanoparticle diameter by the simple adjustment of an applied voltage. Using this method we have created layers of Al2O3 containing well-separated, size-selected ZnO nanoparticles with areal densities between 10^{10} and 10^{12} cm^{-2}. We are now focusing on Atomic Force Microscopy studies comparing samples
containing only ZnO nanoparticles and samples in which nanoparticles were encapsulated by Al₂O₃ deposition. Photoluminescence measurements on these films are also underway in an attempt to probe the optical properties of continuous ZnO films. Our main focus is on the identification of size effects and interface phenomena in these nanostructured ZnO samples.

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High School Teacher Involvement
Title: Research Experiences for Undergraduate Students at UAB
Student: Debbie Anderson (Jefferson County International Baccalaureate, Birmingham, Alabama)
Advisor: James C. Martin

During summer 2003 high school teacher Debbie Anderson was involved with research performed in the laser deposition facility funded by this MRI award. Among her research activities, Ms. Anderson documented on video the activities of undergraduate students performing research. This is leading to the creation of new audiovisual materials (in digital video format) that can be used in high school classrooms to introduce students to how materials research is carried out in academia. Ms. Anderson worked in close collaboration with undergraduate student Gregory Davis developing a well crafted explanation at the level of high school science of his undergraduate research project on nanoengineered metallic surfaces (see Undergraduate Project 3 previously described).