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14. ABSTRACT Over course of this project, the objective has evolved based on the results obtained. In the original proposal, our objective was basically to study the interaction between the incident laser and the multiphase materials that are used in laser direct write deposition in order to produce metastable phases of materials for improved performance in a variety of applications such as energy storage and corrosion resistant systems. Based on our results described below, we extended this study in two significant ways. In the first modification, we have begun to develop a method based on a thick polymer absorbing layer to isolate the effects of mechanical and thermal stress on the transferred materials. In the second extension, we have developed methods to rapidly shape the intensity profile of the incident laser and begun preliminary studies on the effects of shape on the material response. Both of these important extensions were supported in part by AFOSR and will be continued in future studies.					
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AFRL-SR-AR-TR-08-0235

Final Progress Report: "Thick Film Metastable
Materials via Laser Processing"

PI: Craig B. Arnold
Princeton University

PM: Dr. H. Schlossberg
AFOSR Grant # F9550-05-1-0406
Start Date: June 15, 2005
End Date: March 31, 2008

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Objectives: Over course of this project, the objective has evolved based on the results obtained. In the original proposal, our objective was basically to study the interaction between the incident laser and the multiphase materials that are used in laser direct write deposition in order to produce metastable phases of materials for improved performance in a variety of applications such as energy storage and corrosion resistant systems. Based on our results described below, we extended this study in two significant ways. In the first modification, we have begun to develop a method based on a thick polymer absorbing layer to isolate the effects of mechanical and thermal stress on the transferred materials. In the second extension, we have developed methods to rapidly shape the intensity profile of the incident laser and begun preliminary studies on the effects of shape on the material response. Both of these important extensions were supported in part by AFOSR and will be continued in future studies.

Status of Effort: This grant expired March 31, 2008 after 2.5 years of effort. The status of each phase identified in the original proposal is summarized:

Phase I: Proof of principle and characterization of metastable materials: This part of the project has been completed

Phase II: Detailed comparison to other laser surface treatments: This part of the project has been started with some preliminary results obtained. Based on results from phase I, we shifted some our attention from Phase II toward probing the underlying mechanism of material transformation through beam shaping and thick film absorbing layers.

Phase III: Development of applications in coatings and energy storage: This part of the project has been started with preliminary results obtained. Based on results from phase I, we shifted some our attention from Phase II toward probing the underlying mechanism of material transformation through beam shaping and thick film absorbing layers.

Extension to thick film polymer layer: In the original proposal, we examined the effects of direct laser irradiation in the multicomponent inks and the subsequent modifications to the material properties. However, by including a dynamic release layer (DRL), it is possible to further probe the fundamentals of the laser interactions. Standard DRL's rely on thin metal layers that absorb the incident optical energy and rapidly ablate leading to forward transfer. By using a thick polyimide film, the laser is still absorbed in the layer, but in this case, incomplete ablation of the layer leads to rapid deformation of the remaining polyimide layer leading to transfer. Through this technique, there is still momentum transfer, but the thermal effects can be significantly curtailed. During the last year, of this grant, we have begun to examine this approach in delicate materials which are sensitive to thermal and mechanical damage. This extension was partially supported by funding from NSF.

Extension to beam shaping devices: In the original proposal, we limited our incident laser interactions to traditional Gaussian beams. However, through thermal modeling of the laser interaction, we recognized that the intensity distribution could play an important role in shaping the material interactions. One of the limitations in beam shaping approaches is that they are too slow to adaptively shape a beam from pulse to pulse in a

laser direct writing application. Therefore, we developed a new devices based on acoustic driven index of refraction variations in a cylindrical system. Through this method, we were able to provide Bessel and annular beam shapes to materials processing. This extension was partially supported by funding from Princeton University.

Accomplishments/New Findings:

Over the course of this grant, our progress has been steady in providing us with a variety of new findings and results that are consistent with the original goals of this work. Although there were a number of results and findings, I briefly summarize the 3 most significant of them:

1) Incident laser can provide enough energy to cause the formation of improved electrochemical materials: The first phase of this work was intended to identify this effect and to understand and control this effect. Our main results confirm this effect and demonstrate that the resulting material exhibits improved performance in energy storage and conversion applications. Initial studies showed that as the laser energy is increased, there is an increase in local sintering of the particles in the multiphase materials in the case of Titanium Dioxide and Hydrous Ruthenium Oxide. This leads to better transport properties in the porous electrode material and improved performance. However, the more surprising result is that as the laser energy increases further, *there is actually less sintering*. Although this result seems counterintuitive, the reason for this behavior is related to the hydrodynamic expansion of the multiphase material. After the laser interacts with the ink, there is an expansion of the ink as it flies toward the receiving substrate. During this transfer process, there is cooling to the material. By performing in situ imaging of the transferring material, we can see that as the laser energy increases, not only does more energy get absorbed by the material, but the deposition process is more explosive. This results in additional cooling during the transfer process due to increased surface area and higher material velocity. Therefore, beyond a certain material dependent limit, there is a reduction in this effect.

2) Effects of thick film polymer absorbing layer for transfer studies: By implementing a laser absorbing layer between the supporting transparent substrate and the multiphase ink, it is possible to isolate the optical energy from the ink material. Traditional methods employing metal films sufficiently block the UV light, but they do not prevent the transfer of heat and mechanical energy into the ink. Rather, we developed a method based on a thick film polyimide in which the thickness of the polymer film is significantly larger than the absorption length of the laser. The resulting film is partially ablated and the expansion of this vapor results in the mechanical deformation of the polyimide film and therefore the transfer of multiphase ink. In this manner, we can isolate the effects of thermal energy on the multiphase ink compared to the mechanical shock induced phenomena. With the support of this grant, we have implemented this approach experimentally to delicate materials such as organic semiconducting molecules and biological systems such as embryonic stem cells with great success. In addition, we have recently begun modeling the physics and mechanics of this system to further understand the mechanisms of material modification and transfer.

3) Rapid beam shaping: Using the support of this grant, we have developed a tunable device capable of providing intensity patterns for materials processing. We call this device the tunable acoustic gradient index of refraction lens (TAG) lens. This device works by propagating a sound wave through a refractive fluid. Local density variations lead to index of refraction differences causing bending of the light and ultimate pattern formation. Since it is based on acoustic waves, the speed of this device is quite fast relative to other beam shaping devices such as spatial light modulators. We have extensively modeled and characterized this device and have begun to implement it for materials processing. Our initial results indicate that not only does it work as desired for pattern formation, but it can also be used as a rapid varifocus lens for imaging and confocal applications. This device has shown great potential and has resulted in multiple papers, patent disclosures, and one patent filed. In addition, we have been in talks with a number of companies with respect to licensing of this technology. With respect to this grant, the initial results indicate that beam shape play an expected role in the materials modifications, but additional studies are required to fully understand the effect of non-Gaussian beams and the resulting material properties.

Personnel Supported: Graduate Students: Guodan Wei (MSE), Euan McLeod (PhD), Nick Kattamis (PhD). Post-doc: Alex Mermillod-Blondin (PhD. St. Etienne-Jean Monet University)

Publications acknowledging support of this Grant:

- A. Mermillod-Blondin, E. McLeod, and C. B. Arnold, "Dynamic pulsed-beam shaping using a TAG lens in the near UV" *In Press, Appl. Phys. A.* (2007)
- C. B. Arnold and E. McLeod, "A new approach to adaptive optics for materials processing: Acousto-optic beam shaping brings a new dimension to adaptive optics" *Photonics Spectra*, 41(11), 78-84 (2007) (Invited)
- N. Kattamis, P. Purnick, R. Weiss, and C. B. Arnold, "Thick-Film Laser Induced Forward Transfer for Deposition of thermally and mechanically delicate materials", *Appl Phys. Lett.*, 91, 171120 (2007)
- E. McLeod and C.B. Arnold, "Mechanics and refractive power optimization of tunable acoustic gradient lenses," *J. Appl. Phys.* 102, 033104: 1-9 (2007) C.B. Arnold, P. Serra, and A. Pique "Laser direct write of complex materials", *MRS Bulletin*, 32 23-31 (2007)
- C.B. Arnold and A. Pique, "Laser Direct Write Processing" *MRS Bulletin*, 32, 9-11 (2007)
- E. McLeod and C. B. Arnold, "Complex beam sculpting with tunable acoustic gradient index lenses", in *Complex light and optical forces*, ed. D. L. Andrews, International Society for Optical Engineering (SPIE), 6483, 64830I (2007) E. McLeod, A. B. Hopkins, and C. B. Arnold, "Multiscale Bessel beams generated by a tunable acoustic gradient index of refraction lens", *Opt. Lett.*, 31, 3155-3157 (2006)
- T. Tsai, E. McLeod, and C.B. Arnold, "Generating Bessel beams with a tunable acoustic gradient index of refraction lens", in *Optical trapping and Optical*

Micromanipulation III, eds. K. Dholakia and G. Spalding, International Society for Optical Engineering (SPIE), 6326, 63261F (2006)

Interactions/Transitions:

Presentations: A number of invited talks at universities have been given during the course of this grant that acknowledge some of the results obtained through this funding. These include: William Patterson College, George Washington University, City College of NY, Haverford College, Yale University, Columbia University, University of Barcelona, ETH/Zurich, Rhode Island College, and University of Michigan.

In addition, 2 invited talks at international conferences were given on aspects related to this grant.

FLAMN-07, St. Petersburg Russia

LASERION 2007, Schloss-Ringberg, Germany

Finally, contributed talks by the PI and associated students were presented at CLEO 2008

APS March meeting 2008

COLA 2007

LPM 2007

LAMOM, Photonics West 2007

MRS Fall meeting 2006

ECS October meeting 2006

MRS Fall meeting 2005

Consultative functions: NONE

Transitions: A number of discussions were undertaken based on the development of the TAG lens however, to date, there have not been any contracts signed

New Discoveries/Inventions: Over the course of the extension toward rapid beam shaping, we have made two disclosures to the Intellectual property office at Princeton. Both of these disclosures are related to the development of the TAG lens and the use of the tag lens in imaging applications.

Patents filed, disclosures filed Based on the two disclosures, one US Patent has been filed. The complete reference is: C.B. Arnold, E. McLeod, and A. Mermillod-Blondin, "Tunable acoustic gradient index of refraction lens and system" US Patent application, filed Feb 25, 2008

Honors/Awards: A graduate student, Euan McLeod won the best Graduate student award at the COLA 2008 conference for his presentation on work related to this grant.