# Mechanisms of Resonant Infrared Pulsed Laser Ablation and Deposition of Polymers

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*ABSTRACT: Recent research results obtained from a visit to the Paul Scherrer Institute in Switzerland are described. The deposition of silver nanoparticle films and subsequent optical and physical characterization is discussed. The experiences of the PI, postdoctoral fellow, and undergraduate student are discussed along with "lessons learned."*

## INTRODUCTION

Thin polymer films have an extraordinary range of applications areas, from antistiction to microelectronic to bicompatible coatings. Unfortunately, there are relatively few general methods for producing these films that satisfy all of the requirements of the applications, partcularly when multiple layers are neccesary. At Rutgers-Camden under the auspices of NSF Award DMI-0613837, the use of laser ablation is explored as a general method for the deposition of thin polymer films[1]. Here, a laser that is tuned to a vibrational band in the polymer target is used to produce polymer vapor. The polymer to be deposited is pressed into a pellet and placed on a rotating stage in a vaccum chamber. A substrate is placed in the path of the vapor and a thin film deposits uniformly. Our results have shown that it is possible to deposit certain polymers with a minimum of decomposition by this technique.

Nanocomposite polymer-metal films have a wide range of applications. In particular, our interest in them stems from the possibility of producing novel optical materials. The most celebrated application for nanocomposites is the production of metamaterials. Metamaterials are are produced when two (or more) pure materials are mixed that have different dielectric constants and magnetic susceptibilities. The composite has properties of both materials and as long as the characteristic length of each domain is small compared with the electromagnetic radiation, the composite material will appear as a homogeneous material to an incoming light wave. In this fashion, materials can be designed and structured that do not exist naturally. The holy grail of metamaterials is a material with negative index of refraction – in principle, one could create cloaking devices with such materials. Our initial interest in these materials

centers, however, on the imaging properties of nanocomposite thin films. For example, thin films of silver nanoparticles may be used to produce a lens[2]. Not only can the usual limitation of observable feature size of refractive optics be overcome (diffraction limit), but the abberation errors can be eliminated as well because the optical element is flat instead of curved.

The Paul Scherrer Institute (PSI) is the largest federal laboratory in Switzerland that funds basic research. It is within a half hour train ride from Zurich and enjoys close cooperation with ETH-Zurich. Dr. Thomas Lippert is head of the Materials Group in the General Energy Research Department. His rsearch interests include thin film deposition and laser ablation of polymers, so he made a natural choice for a collaborator. In particular, PSI possesses all of the facilities required for the deposition of high quality thin films and subsequent characterization. Rutgers-Camden has the required optical characterization equipment to successfully carry out the project.

The purpose of the trip that was funded by an IREE supplement to this award was twofold. First, we intended to perform plume shadowgraphy experiments with the $CO_2$ laser possessed by Dr. Lippert's group to compliment our existing data. Second, we intended to deposit silver nanoparticle thin films in order to study the optical properties of such films. It is our intent to combine silver nanoparticles with polymer films in order to explore the possibility of novel optical materials.

The travelers will nclude two researchers for Prof. Bubb's laboratory, a postdoctoral fellow, Ullas Gurudas and an undergraduate research assistant, Elijah Brookes. The dates of travel were 5/15/2007-8/15/2007.

## RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

The program of research centered on two experiments: plume shadowgraphy with the $CO_2$ laser and the growth of silver nanoparticle thin films. Unfortunately, everything that could go wrong with the $CO_2$ laser did, and the researchers spent much of the summer troubleshooting it and fixing the laser. Although they gained valuble experience, it was frustrating not to obtain the intended data. Nevertheless, we gained more insight into this particular technique and have begun to assemble the same experimental set up in our home laboratory. We have committed to completing the experiments this year with the researchers from PSI.

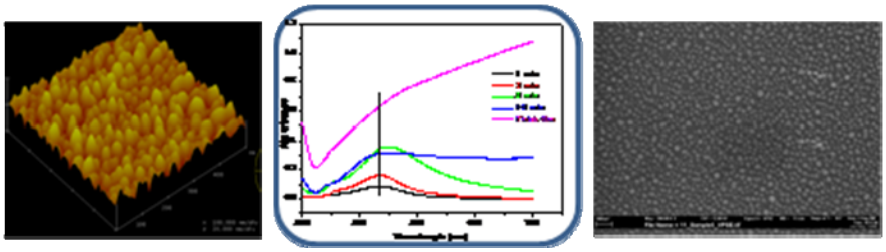

**Figure 1 - (a) AFM scan of silver nanoparticle film (b) surface plasmon resonance near 410 nm, and (c) SEM micrograph of film.**

The second set of experiments fared far better. We were able to deposit high quality thin films of silver nanoparticles. The key signature that we were looking for was

a surface Plasmon resonance at around 410 nm. In Figure 1 we display an AFM scan, SEM micrograph, and a UV-Vis spectrum of the deposited films. Our results demonstrated that we can control the size and in some cases the orientation of the nanoparticles. Subsequent nonlinear optical characterization has revealed that the films exhibit optical limiting and other nonlinear optical properties.

These results will help us to explore new frontiers in our research program. In particular, we will investigate the growth an optical properties of nanocomposite polymer-metal thin films. Our prior research on the growth of polymer films will inform these efforts.

The guest researchers were treated as part of the host's research group. They ate lunch every day with the group and attended both weekly group meetings and seminars. During "down" time, Mr. Brookes helped a Ph.D. student write her dissertation in English as her native language is German. PSI has on-site housing for guest researchers and is located in the scenic Aurau region of Switzerland, so there was little time lost to commuting to the lab and meals were provided by the laboratory as well.

## BROADER IMPACTS OF THE INTERNATIONAL TRAVEL

This research project certainly helped us to broaden the scope of the original award and brought us in a new direction. Our interest in metamaterials and nanocompostes was the driving force. It is gratifying to note that much of what we have already learned is applicable to the growth of polymer-metal nanocomposite thin films.

The success of this initial work has encouraged new cooperation between our research group and Dr. Lippert's. In particular, one of his graduate students (S. Heroith) has closely cooperated with Dr. Gurudas, the posctdoctoral researcher. We are planning a new set of film growth experiments, and the Mr. Heroith will grow these films for us. His prior involvement and interest in the research will be a great asset in cementing the collaboration.

The experience was very positive for Mr. Brookes as well. He faced many challenges during his trip, not the least of which was contracting Lyme's disease during his second week. This is a serious disease and limited his ability to meaningfully participate for two to three weeks. Perhaps more challenging was the culture shock, not of being in a different country, but of being in a somewhat corporate environment with a fixed schedule. The PI's research group is much more informal, as it centers on undergraduates. The undergraduate students are used to the pace of research being dictated by their ability to understand and meaningfully participate. The research group at PSI is geared towards the Ph.D. students, and while they were extremely helpful, they did not have time to continually stop and explain the details of every experiment or apparatus to Mr. Brookes. This was somewhat of a shock and by his account somewhat overwhelming. However, the experience broadened his perspectives and did not dissuade him from his goal of going to graduate school in Physics, so it was a positive experience.

Dr. Gurudas gained experience in close mentoring of undergrates. It was the PI's intent to pair the undergraduate student with a postdoctoral fellow in order to ease the burden on the undergraduate. Initially, it was planned for the postdocotoral fellow to travel one month earlier than the student in order to set up the equipment and to get the experiments smoothly running before the student's arrival. However, circumstances did not permit this and they wound up arriving at the same time.

The close proximity to Zurich allowed for many trips to the city as well as the outlying areas. The host group's students were very gracious in entertaining.

## DISCUSSION AND SUMMARY

There were invaluable lessons for the undergraduate student, postdoctoral fellow, and PI in this international research experience. As detailed above, the undergraduate, Mr. Brookes, gained a new perspective on research and the pace tht is expected at the next level. The postdoctoral fellow gained lessons in effective mentoring and the PI learnedlessons in planning and communication. For example, the PI would have preferred the postdoctoral fellow to precede the undergraduate student by at least one month. The amount of time lost to the CO2 laser was frustrating as well and it would have been helpful to ask more questions about the operation and state of the equipment before traveling.

Despite the setbacks in one area, we were extremely successful in the deposition of silver nanoparticles and the growth and characterization of these films was uneventful. The PI considered this to be a particularly good lesson for Mr. Brookes. On paper, what was a relatively straightforward experiment (plume shadowgraphy with the $CO_2$ laser) turned out to be nightmarishly difficuly because of electronics problems along with problems with the tube. On the other hand, the experiments with the growth of the silver nanoparticle films went very smoothly despite the fact that this was a new area for all of us. These results will certainly yield several publications and form the basis for at least one grant application.

As for best practices, the most important thing seems to be communication. In retrospect, the PI feels that weekly or even biweekly conference calls would have been beneficial – or at least a three way chat online. This approach would have been much more frtuitful than speaking to both researchs separately by email daily. The PI also learned valuable lesson concerning communication with the host particularly where equipement is concerned.

## ACKNOWLEDGEMENTS

Include any relevant information including:

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## REFERENCES

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## BRIEF BIOGRAPHIES OF RESEARCHERS

**Daniel M. Bubb** received the B.S. degree in Physics from Ursinus College in 1993. He received his M.S. degree in Physics from Florida Institute of Technology and Ph.D. degree in Applied Physics from New Jersey Institute of Technology in 1995 and 2000, respectively. He spent 20 months at the Naval Research Laboratory as an American Society for Engineering Education Postdoctoral Fellow before becoming an Assistant Professor in the Department of Physics at Seton Hall University. In 2005, he moved to the Department of Physics at Rutgers University on the Camden campus where he was promoted to Associate Professor with Tenure in July of 2006.

**Ullas Gurudas** received B.Sc. and M. Sc from Kerala University, India in 1983 and 1986. He received his Ph. D. Degree in Physcis from Banaras Hindu University (BHU), Varanasi, India in 1992. He was a post-doctoral fellow at Physical Research Laboratory Ahmedabad, India and Research Associate in BHU. He has been an Assistant Professor at Center for Laser Spectroscopy, Manipal, India during 1998-2002. He moved to US in 2002 and was a post-doctoral Associate at the Chemistry department of New York University. Since 2006, he has been a post dotoral associate at the Physics Department of Rutgers University at Camden. Research interests include Laser spectroscopy, Laser material material interactions.

**Elijah Brookes** is a B.A. student dual majoring in Physics and Mathematics at Rutgers-Camden University.