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14. ABSTRACT

The funded instrumentations were essential to the continuation of the project and were integrated in the existing PLD system which was funded by other AFOSR grants. The project studies the feasibility of producing functional polymer nanocomposite films for light emitting applications using the new double pulsed laser deposition (DPLD) technique. The existing pulsed laser deposition vacuum chamber has been modified to accommodate two laser beams of different wavelengths for the in-situ ablation of two targets: a polymer host and a rare-earth (RE) highly efficient upconversion emitting inorganic dopant. Special provisions were made for cooling the target to control the ablation of the polymer without interrupting the process. Nanocomposite films of acrylic polymer and nanoparticles of the compounds of the rare earth elements were fabricated by the proposed method with near- infra-red laser radiation (1064-nm wavelength) ablating the polymer targets and visible radiation (532 nm) ablating the inorganic targets. The fabricated nanocomposite films were characterized using funded atomic force microscopy, X-ray diffraction, optical fluorescence spectroscopy, and visual observation of the fluorescence. It was discovered that the produced polymer nanocomposite films retained the crystalline structure and the upconversion fluorescence properties of the initial rare earth compounds mainly due to the better control of the deposition process of the materials of different nature. The proposed method can be used for making a wide variety of composite films.

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Executive summary

Significant accomplishments. The funded instrumentations were essential to the continuation of the project and were integrated in the existing PLD system which was funded by other AFOSR grants. The project studies the feasibility of producing functional polymer nanocomposite films for light emitting applications using the new double pulsed laser deposition (DPLD) technique. The existing pulsed laser deposition vacuum chamber has been modified to accommodate two laser beams of different wavelengths for the in-situ ablation of two targets: a polymer host and a rare-earth (RE) highly efficient upconversion emitting inorganic dopant. Special provisions were made for cooling the target to control the ablation of the polymer without interrupting the process. Nanocomposite films of acrylic polymer and nanoparticles of the compounds of the rare earth elements were fabricated by the proposed method with near- infra-red laser radiation (1064-nm wavelength) ablating the polymer targets and visible radiation (532 nm) ablating the inorganic targets. The fabricated nanocomposite films were characterized using funded atomic force microscopy, X-ray diffraction, optical fluorescence spectroscopy, and visual observation of the fluorescence. It was discovered that the produced polymer nanocomposite films retained the crystalline structure and the upconversion fluorescence properties of the initial rare earth compounds mainly due to the better control of the deposition process of the materials of different nature. The proposed method can be used for making a wide variety of composite films.

Problem encountered. (1) Polymer composite film deposited on the substrate by DPLD remained to be hot and in liquid form. It had a tendency to flow down driven by gravity. An adequate substrate cooler has to be designed and built to solidify the deposited polymer and improve the uniformity of the film. (2) Though visible observation revealed no coloration of the polymer film deposited by the proposed DPLD method indicating polymer decomposition, a comprehensive FTIR absorption spectroscopy has to be conducted to analyze the integrity of the molecular structure of the deposited polymer and the extend of possible molecular dissociation. (3) Though preliminary XRD data as well as visual observation of the upconverted visible emission of the composite films of the polymer and the RE fluorophores provided very encouraging evidence of the successful transfer of the RE fluorophores in the resulting films without substantial disintegration, a comprehensive and systematic XRD and fluorescence spectroscopy is needed to evaluate the extent of possible disintegration and modification of the RE fluorescent compounds during the DPLD process. (4) Apparently it is hard to estimate at the present moment how nano- the fabricated composite films are (only indirectly through XRD). The films must be analyzed directly with the high-resolution transmission electron microscopy (HR TEM) to measure the size of the RE particles incorporated in the polymer matrix.

Future plans. (1) To design and fabricate the substrate cooler for the proposed DPLD system. (2) To conduct systematic FTIR spectroscopic study with the acquired FTIR spectrometer of the produced polymer composite films and evaluate the extent of the polymer dissociation encountered during the proposed DPLD process against the conventional single-beam PLD. (3) To conduct systematic XRD study with the acquired instruments and the laser activated fluorescence spectroscopy (with 980-nm laser source) of the fabricated composite films and evaluate the extent of possible disintegration and crystalline modification of the

RE upconversion compounds during the proposed DPLD process against the conventional single- beam PLD. (4) To conduct systematic high-resolution TEM study of the fabricated composite films and evaluate the size and shape of the RE fluorescent particles embedded in the polymer matrix during the proposed DPLD process. (5) To design another PLD chanber which will have double acces windows in opposite direction of the chamber to accommodate the two different laser beams from opposite direction to maximize the overlap of the two plumes and produce more effective homogeneous nanocomposite thin film by using the new invention of the double movement stages of the target holder. This is an essential part of the investigation (6) To finalize filing the patent application for the proposed multi-beam PLD method and apparatus. (7) to publish the new results of the nanocomposite sensor, FTIR, XRD and XRF data.

Figure captions

Figure 1. (a) General view of the experimental setup of the PLD system. (b) Top view of the PLD system, which shows the laser beam with respect to the target (blue line). The second laser is directed at an angle of 2 degrees with respect to the first one in the modified DPLD system in order to have the plume of the second target overlapping the first plume.

Figure 2: Schematic diagram of the modified double target holder. Target 2 has a variable tilt to provide overlapping of the plumes from both targets of the substrate.

Figure 3. Fluorescence spectrum of $NaYF_4$: Er^{3+}, Yb^{3+} powder (compound "a") illuminated with 980-nm laser radiation.

Figure 4. Fluorescence spectrum of $NaYF_4$: Tm^{3+}, Yb^{3+} powder (compound "c") illuminated with 980-nm laser radiation.

Figure 5. AFM scan of the composite film of PMMA: $NaYF_4$: Er^{3+}, Yb^{3+}.

Figure 6. AFM scan of the composite film of PMMA: $NaYF_4$: Tm^{3+}, Yb^{3+}.

Figure 7. XRD spectrum of the composite film of PMMA:$NaYF_4$:Ho^{3+},Yb^{3+}.

Figure 8. XRD spectrum of the powder of $NaYF_4$:Ho^{3+},Yb^{3+} baked at 400^oC.

Figure 9. XRD spectrum of the composite film of PMMA:$NaYF_4$:Tm^{3+},Yb^{3+}.

Figure 10. XRD spectrum of the powder of $NaYF_4$:Tm^{3+},Yb^{3+} baked at 400^oC.

Table titles

Table 1. Comparison of the observed emission from the composite films prepared by the DPLD method against the emission produced by the initial RE powders

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1. Introduction

Since the work of Dijkkamp et al [1], the pulsed laser ablation (PLD) technique has been intensively used for deposition of many kinds of oxides, nitrides, carbides, and metals and for fabrication of thin films including those composed of electro-optic $BaTi0_3$, piezoelectric ZnO, electroconductive $Ti0_2$, rare-earth (RE) doped phosphate glasses etc. [2-14] Those thin films had many deficiencies that had to be addressed before making them suitable for commercial applications. The technique was also used by Smith and Turner [2] in 1965 for the preparation of semiconductor and dielectric thin films. They demonstrated the stoichiometry transfer between the target and the deposited film and high deposition rates of about 0.1 nm per pulse. The occurrence of the droplets of the target material on the substrate surface has been observed in Ref. 3. Despite some encouraging results for single-component films, the conventional PLD technique remains to be poorly suitable for composite films, particularly those made of polymer -inorganic compounds. One of the reasons is that both, the polymer and the inorganic dopant , cannot be simultaneously brought to the substrate with the laser beams properly adjusted for each component . This project deals with a new variant of PLD called the double pulsed laser deposition (DPLD) that treats the organic host material and the inorganic dopant simultaneously with two different laser beams producing overlapping plumes. It is expected that the proposed method will bring improvements to the PLD technique especially when dealing with hard coatings, such as boron nitride [15], carbon nitride [16], and diamond-like carbon [17]. In these cases, the energetic nature of the depositing vapor could enable the growth of the desired hard phases, which are not thermodynamically stable under the growth conditions of the conventional approach [18 - 23].

2. Experimental

2.1. Pulsed laser ablation/deposition chamber

The PLD system (Fig.1) consists of a spherical vacuum chamber (12-inch diameter), which has the target carrousel facing the substrate holder with the distance between them varying within 2-3 cm. The deposition carrousel is mounted on a rail assembly that is controlled by a computer. This enables the selection of the targets during the ablation process, and also the selection of dopant materials. This setting provides for up to 0.15-m travel distance of the targets that can be quickly swapped. The chamber has multiple optical quartz windows of a 4-in and 6-in diameter for multiple ablating laser beams. The spare windows can be conveniently used for the visual inspection of the targets during the alignment. Additionally, the vacuum chamber has a Reflected High Energy Electron Diffraction (RHEED) system attached. The system can be used for in-situ monitoring of the film growth. All six targets rotate simultaneously at the same speed. For ion extraction, a grid assembly with a 0.625-inch hole is placed right in front of the 0.5-inch substrate holder. By adjusting the ablation parameters, such as the laser power and fluence, the ionization rate in the ablation plume can be controlled. The conventional PLD chamber design is modified to accommodate the double target holder. This target holder allows two laser beams to ablate two different materials in-situ. This approach is the essence of the proposed Double Laser Pulsed Deposition (DPLD). The double target is split in two separate mechanical stages (Fig. 2) holding individual targets of 0.5-inch diameter each. Both stages can be tilted independently at different angles to allow the plumes of the two targets to overlap and interact in order to produce a thin film with desirable properties. This new design of the target holder is expected to overcome the limitations of the conventional PLD, particularly, when dealing with composite polymer-inorganic films.

2.1. Deposition configuration

Fig. 2 presents the schematic of the modified target holder, which accommodates two separate targets for two laser beams. Two plumes are formed using two separate laser beams with different wavelengths. The laser beams are applied in situ to two targets and the energy and fluence of the laser beams are adjusted to optimize the deposition process. One half of the new target holder (for Target 2) can be tilted in order to control overlapping of the two plumes and their interaction near the substrate.

2.2. Deposition procedure

A sample of the solution of polymethyl(methacrylate) known as PMMA in chlorobenzene at a proportion of 1 g solids per 10 mL liquids was poured in a copper cup and frozen in liquid nitrogen. Then the copper cup with the frozen polymer solution was mounted on a double target holder (as Target 1) cooled with continuous flow of liquid nitrogen. Target 2 was made of the powder of an upconversion material. The frozen polymer Target 1 was ablated with a 1064-nm laser beam. Target 2 was ablated with 532-nm frequency doubled Nd:YAG beam. Beam 2 (532-nm) was turned ON and OFF in order to control of the proportion of the upconversion material coming in the polymer.

3. Results and discussion

3.1. Upconversion compounds used for the composite film deposition

Three remarkably efficient rare-earth compounds have been developed and incorporated in polymer nanocomposite light-emitting films for micro-lasers using DPLD: (a) $NaYF_4$: Yb^{3+}, Ho^{3+}, (b) $NaGdF_4$: Yb^{3+}, Er^{3+}, and (c) $NaYF_4$: Tm^{3+}, Ho^{3+}. The compounds in powder form were prepared by the wet method followed by high-temperature baking. Compounds (a) and (b) exhibited brilliant upconverted green emission (with up to 10% efficiency) primarily at ~540 nm and compound (c) – red emission (at ~ 650 nm) and blue emission (470 nm) being pumped with an infra-red pump at 980 nm. Fluorescence spectra of compounds (a) and (c) are presented in Figs. 3 and 4.

3. 2. Surface morphology of the composite films produced with DPLD

The surface roughness and the homogeneity of the deposited polymer nanocomposite films: was evaluated using Atomic Force Microscope as shown in Figs. 5 and 6. The AFM scans indicate that the DPLD thin films came out smooth without major defects. This is more likely due to the double plumes interaction. The time of the ablation of the doped materials was well controlled to maintain a doping rate of 5% or less in the thin film. The substrate temperature had the major effect on the structure of the thin film. The higher temperature resulted in more uniform film. The roughness of the surface was measured to be near 50-70 nm for films of 190-270 nm thickness.

3.4. XRD analysis

The DPLD produced composite films were analyzed using X-ray diffraction (XRD) method. Fig. 7 presents the diffractogram of the composite film of PMMA: $NaYF_4{:}Ho^{3+},Yb^{3+}$. For comparison. Fig, 8 presents the XRD spectrum of the initial powder compound of $NaYF_4{:}Ho^{3+},Yb^{3+}$ baked at 400 °C. This sample contains only two phases, hexagonal $Na_{1.5}Y_{1.5}F_6$ and cubic $NaYF_4$. The disordered $Na_{1.5}Y_{1.5}F_6$ is the majority product, but there is a much more equal ratio of the products in this sample (thus the cubic phase is much more prevalent in this sample than in the Tm,Yb-doped sample) compared to the Tm,Yb-doped sample. Here it appears to be about 60/40 in favor of the disordered fluoride. The peaks at 39 and 45 degrees result from the aluminum sample pan. All products are highly crystalline and appear to have particle sizes above 100 nm. One can see a good match between the positions of the diffraction peaks of the composite polymer film and the initial powder compound.

Fig. 9 presents the XRD diffractogram of the PMMA: $NaYF_4{:}Tm^{3+},Yb^{3+}$ thin film at a temperature of 20°C. The diffractogram indicates that the film contains only two phases: hexagonal $Na_{1.5}Y_{1.5}F_6$ and cubic $NaYF_4$. The disordered $Na_{1.5}Y_{1.5}F_6$ is the major product, but the cubic phase is more prevalent in the film than in the initial compound. The proportion appears to be about 60/40 in favor of the disordered fluoride. The peaks at 39 and 45 degrees result from the aluminum sample pan. All products are highly crystalline with an average particle size of 100 nm. For comparison, the XRD spectrum of the initial powder of $NaYF_4{:}Tm^{3+},Yb^{3+}$ baked 400 °C is presented in Fig. 10. This sample is comprised of 3 products: $Na_{1.5}Y_{1.5}F_6$, $NaYF_4$ and YF_3. The main product is $Na_{1.5}Y_{1.5}F_6$. This is actually thought of as the low temperature form of $NaYF_4$, but is not written in that formulation since, crystallographically the Y site is disordered as $Na(Y_{1.5}Na_{0.5})F_6$. This results in hexagonal symmetry (s.g. *P6₃/m*). This material is typically prepared by low temperature techniques (and is the phase synthesized by hydrothermal reactions), and will convert into cubic $NaYF_4$ at 691 °C. This cubic $NaYF_4$ is also present in this sample, but only as a very minor product. The third product is YF_3. All of the products are highly crystalline and probably have diameters greater than 100 nm. The two unassigned peaks at 2-thetas of 39 and 45 degrees are due to exposed aluminum from the sample holder due to the small amount of sample. One can see a good match between the positions of the diffraction peaks of the composite polymer film and the initial powder compound.

3.5. Fluorescence

The prepared comnposite films were illuminated with a 200-mW laser at 980-nm. A fluorescence in green or blue region was observed by the naked eye at room light. The observation results are summarized in Table 1.

Table 1. Comparison of the observed emission from the composite films prepared by the DPLD method against the emission produced by the initial RE powders

N	Composite film	Observed emission from the film	Initial RE-doped compound	Observed emission from the powders
1	PMMA: $NaYF_4$: Er^{3+}, Yb^{3+}	Bright green	$NaYF_4$: Er^{3+}, Yb^{3+}	Bright green
2	PMMA: $NaYF_4$: Ho^{3+}, Yb^{3+}	Weak green	$NaYF_4$: Ho^{3+}, Yb^{3+}	Bright green
3	PMMA: $NaYF_4$: Tm^{3+}, Yb^{3+}	Weak blue	$NaYF_4$: Tm^{3+}, Yb^{3+}	Blue

The results presented in Table 1 together with the XRD data indicate that the proposed DPLD method made possible to transfer the RE compounds in the polymer composite films preserving their structure and the upconversion fluorescence properties fully (row 1 in Table 1) or partially (rows 2 and 3 in Table 1).

4. Significant accomplishments

1. It has been demonstrated for the first time that the proposed new double-beam pulsed laser deposition method made possible to transfer the highly efficient upconversion rare earth inorganic fluorophores in the composite polymer films preserving the rare-earth compound optimal crystalline structure and high-brilliance upconversion emission. This is due to much better control of the deposition process of the materials of different nature. The proposed method thus can be used for fabrication of a wide variety of thin films for light emitters and other applications.
2. The basic components of the new double-beam pulsed laser deposition apparatus and the major process steps have been designed, built, and tested. The preliminary results clearly indicated the advantages of the proposed method. The patent application process for the technology has been initiated.

5. Problems encountered

1. Polymer composite film deposited on the substrate by DPLD remained to be hot and in liquid form. It had a tendency to flow down driven by gravity. An adequate substrate cooler has to be designed and built to solidify the deposited polymer and improve the uniformity of the film.
2. Though visible observation revealed no coloration of the polymer film deposited by the proposed DPLD method indicating polymer decomposition, a comprehensive FTIR

absorption spectroscopy has to be conducted to analyze the integrity of the molecular structure of the deposited polymer and the extend of possible molecular dissociation.

3. Though preliminary XRD data as well as visual observation of the upconverted visible emission of the composite films of PMMA and the RE fluorophores provided very encouraging evidence of the successful transfer of the RE fluorophores in the resulting films without substantial disintegration, a comprehensive and systematic XRD and fluorescence spectroscopy is needed to evaluate the extent of possible disintegration and modification of the RE fluorescent compounds during the DPLD process.
4. Apparently we know very poorly at the moment how nano- the fabricated composite films are (only indirectly through XRD). The films must be analyzed directly with the high-resolution transmission electron microscopy (HR TEM) to measure the size of the RE compounds incorporated in the polymer matrix.

6. Future plans

1. To design and fabricate the substrate cooler for the proposed DPLD system.
2. To conduct systematic FTIR spectroscopic study with the acquired FTIR spectrometer of the produced polymer composite films and evaluate the extent of the polymer dissociation encountered during the proposed DPLD process against the conventional single-beam PLD.
3. To conduct systematic XRD study with the acquired instrument and the laser activated fluorescence spectroscopy (with 980-nm laser source) of the fabricated composite films and evaluate the extent of possible disintegration and crystalline modification of the RE upconversion compounds during the proposed DPLD process against the conventional single-beam PLD.
4. To conduct systematic high-resolution TEM study of the fabricated composite films and evaluate the size and shape of the RE fluorescent particles embedded in the polymer matrix during the proposed DPLD process.
5. To finalize filing the patent application for the proposed multi-beam PLD method and apparatus.

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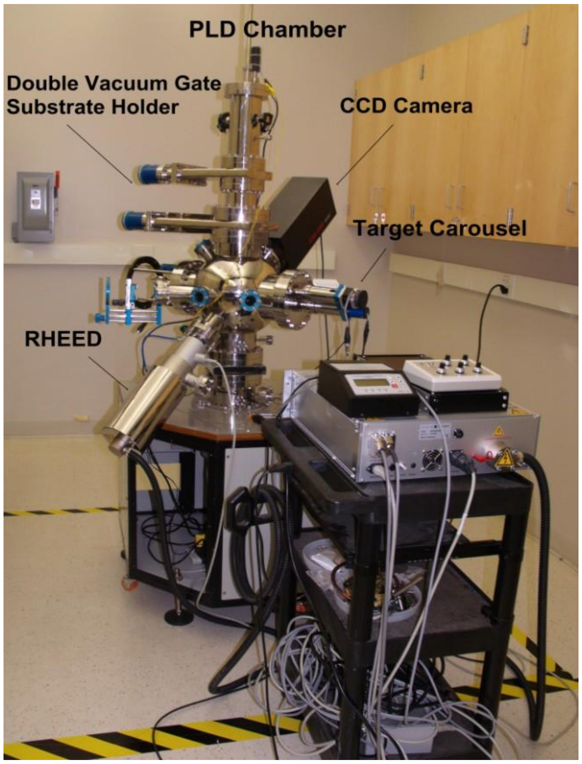
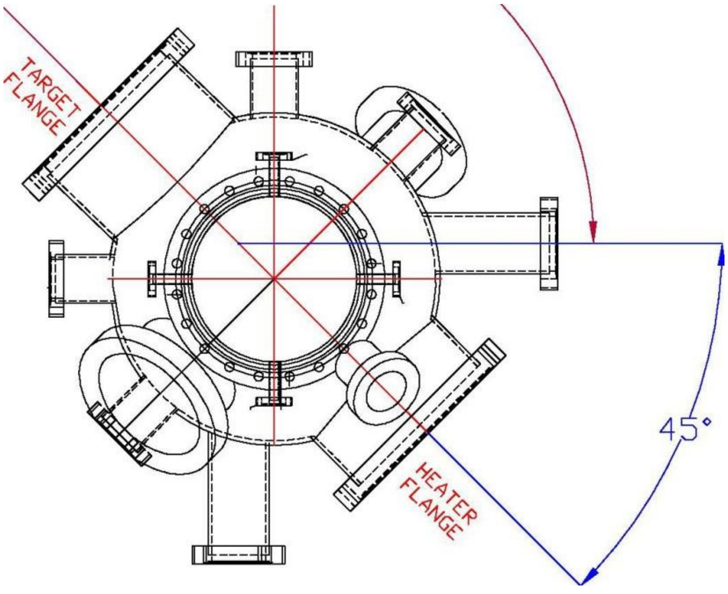
8. Figures



(a)



(b)

Figure 1. (a) General view of the experimental setup of the PLD system. (b) Top view of the PLD system, which shows the laser beam with respect to the target (blue line). The second laser is directed at an angle of 2 degrees with respect to the first one in the modified DPLD system in order to have the plume of the second target overlapping the first plume.

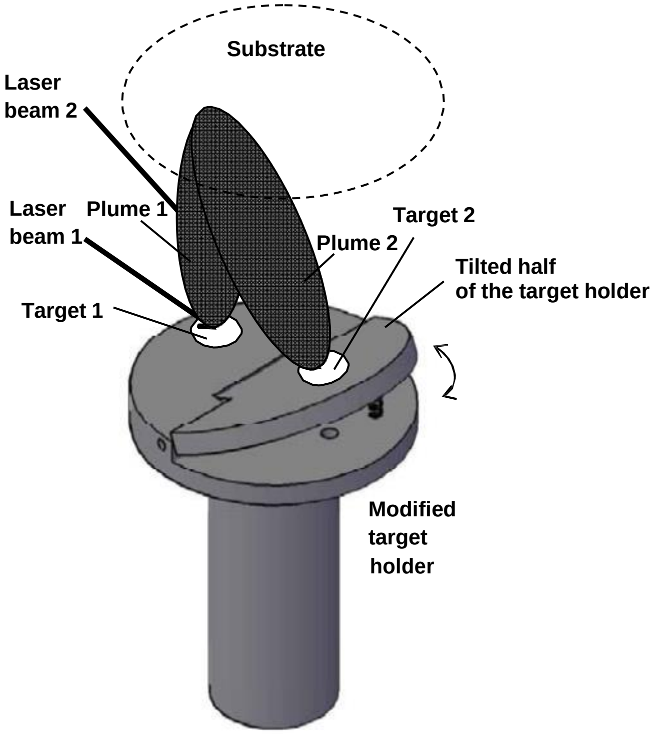


Figure 2: Schematic diagram of the modified double target holder. Target 2 has a variable tilt to provide overlapping of the plumes from both targets of the substrate.

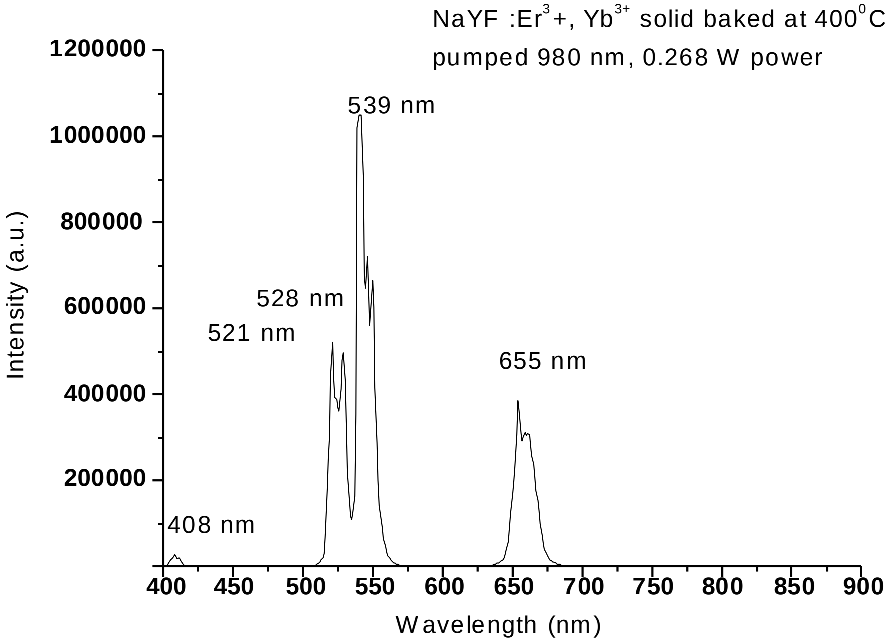


Figure 3. Fluorescence spectrum of $NaYF_4$: Er^{3+}, Yb^{3+} powder (compound "a") illuminated with 980-nm laser radiation.

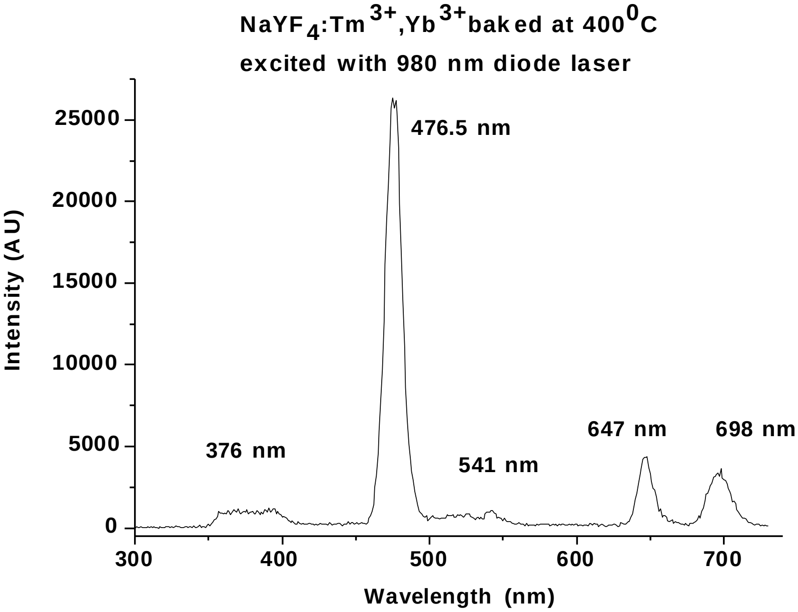


Figure 4. Fluorescence spectrum of $NaYF_4$: Tm^{3+}, Yb^{3+} powder (compound “c”) illuminated with 980-nm laser radiation.

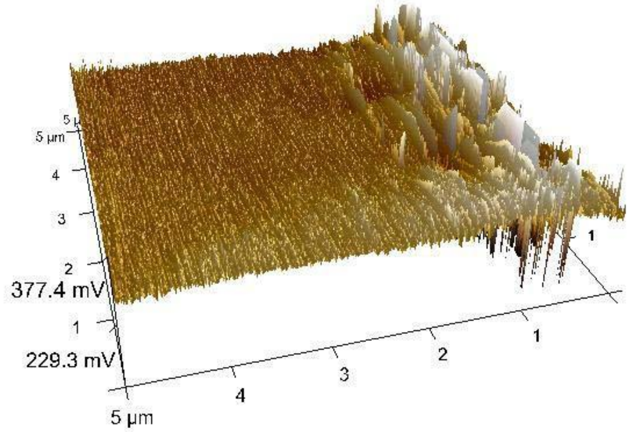
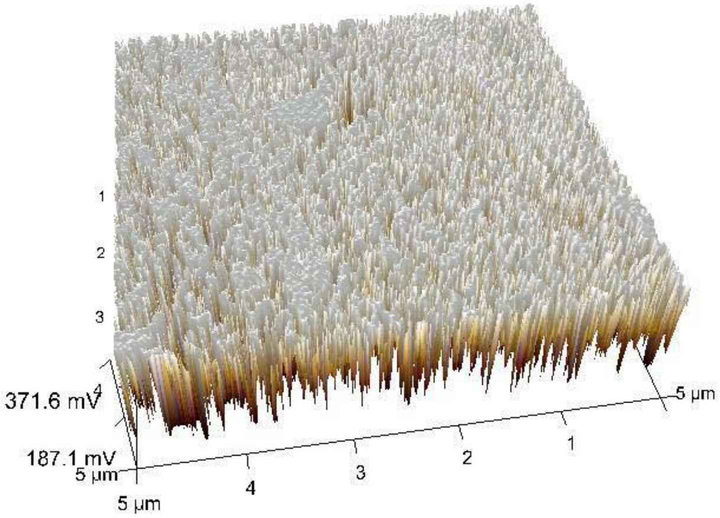


Figure 5. AFM scan of the composite film of PMMA: $NaYF_4$: Er^{3+}, Yb^{3+}.



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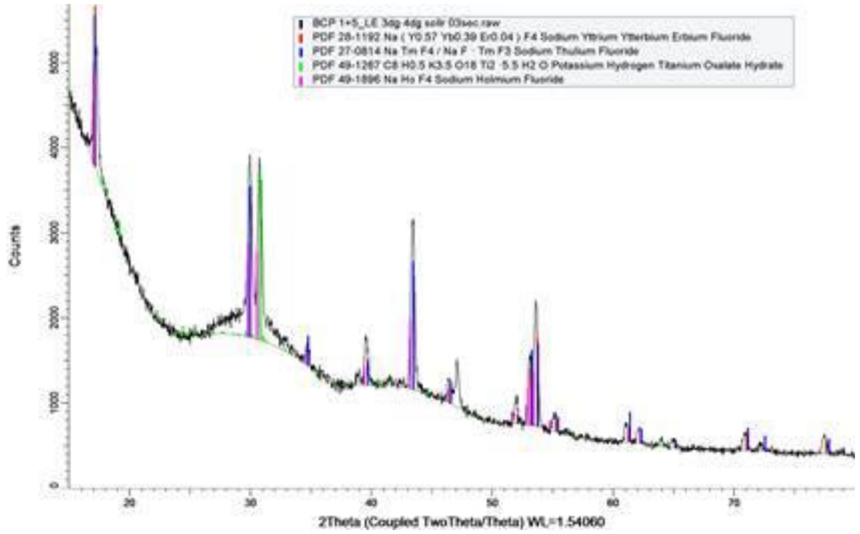

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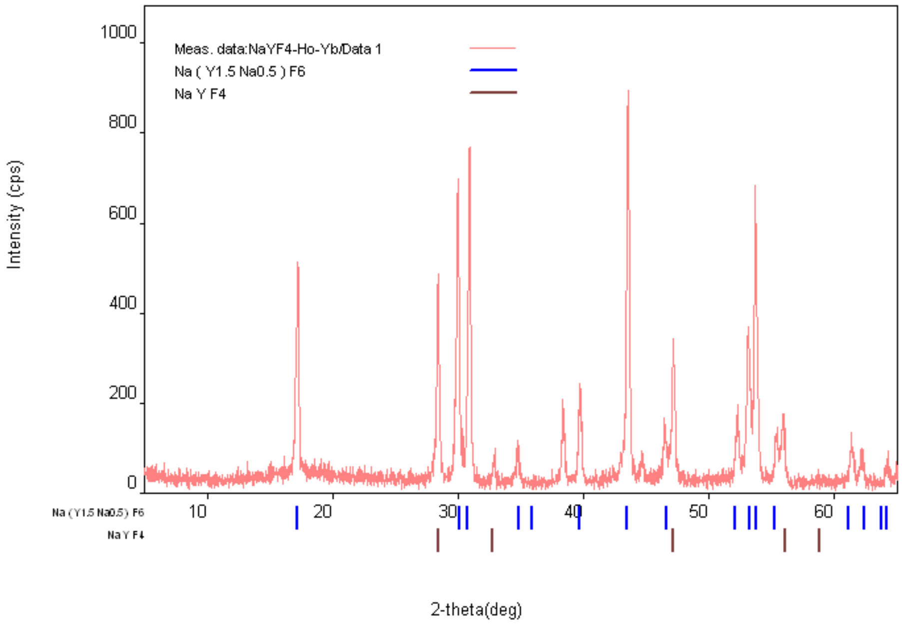

Figure 8. XRD spectrum of the powder of $NaYF_4$:Ho^{3+},Yb^{3+} baked at 400°C.

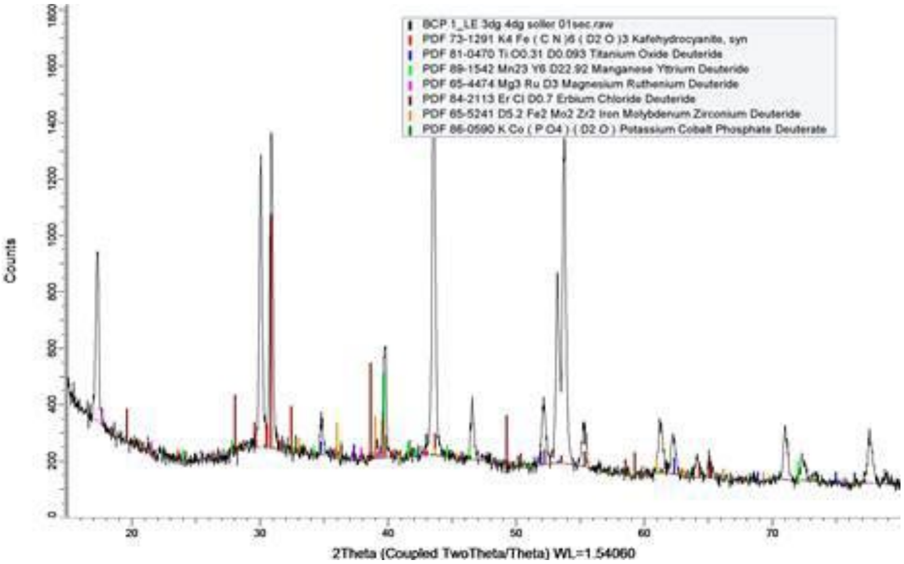

Figure 9. XRD spectrum of the composite film of PMMA:$NaYF_4$:Tm^{3+},Yb^{3+}.

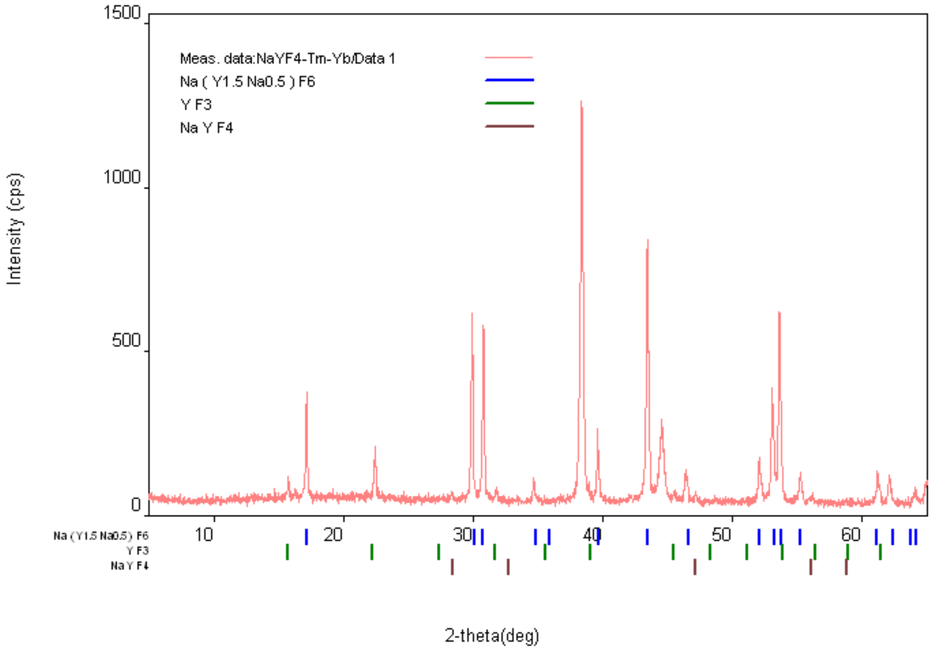

Figure 10. XRD spectrum of the powder of $NaYF_4:Tm^{3+},Yb^{3+}$ baked at 400°C.

9. Participants

Students Participants:
Undergraduate Physics students at Dillard University:

a) Simeon Wilson,
b) Michael Sagapolutele
c) Kimishown Rickerson

Consultants:

a) Dr. Sergey Sarkisov, SSS Technologies, Huntsville, AL
b) Dr. Brent Koplitz, Tulane University, New Orleans , LA

10. Presentations and paper/patent applications submitted/published

Presentations

Student presentations

a. 2013 Emerging Researchers National (ERN) Conference
b. 2012 National society of Black Engineers (NSBE) conference
c. 2012 National Society of Black physicists

Presentation of Dr. A Darwish

Conference chair and Invited talks:

1. **“**Double pulse laser deposition of polymer nanocomposite: NaYF4:Tm3+,Yb3+ films,**”** Invited Oral presentation presenteded 25 August 2013. This conference is a part of SPIE Optical Engineering + Applications , 25 - 29 August 2013 in San Diego, California.

2. “ A new innovative technique for in-situ double ablation of materials for thin film fabrication. Presented at The Twenty first Annual International Conference on COMPOSITES/NANO ENGINEERING (ICCE-21) Tenerife, Spain July 21-27, 2013

Papers published

1. A. Darwish and S. Sarkisov, Method and apparatus for multi-beam pulsed laser deposition of thin films, US Provisional Patent Application No. 61/850,330, February 14, 2013. The full patent is in the processing of filing.
2. A. Darwish, Simeon Wilson, Brent Koplitz, Sergey Sarkisov, DPLD of polymer nanocomposite films for optical sensors and light emitter application, ICCE 21 annual international conference on composite/Nano engineering, July 21-17, 2013, Tenerife, canary
3. Abdalla M. Darwish, Simeon Wilson, Dillard Univ, Sergey S. Sarkisov; L. Darayas N. Patel, Oakwood Univ..Proceedings Volume 8847: Photonic Fiber and Crystal Devices: Advances in Materials and Innovations in Device Applications VII, pp1-14, 2013
4. A.M. Darwish et al Double beam pulsed laser deposition of composite films of poly(methyl methacrylate) and rare earth, fluoride upconversion phosphors. Composites: Part B Engineering, vol 55, pages 139-136 Dec (2013).

Patent application

Abdalla Darwish and Sergey Sarkisov, Method and apparatus for multi-beam pulsed laser deposition of thin films, Provisional US patent Application No. 61/850, 330, filed 02/14/2013.

I am in the process of submitting the full patent. Expected date Jan 25, 2014 if not earlier.

Appendices

A1. Provisional patent application

Description of invention

Title: Method and apparatus for multi-beam pulsed laser deposition of thin films

Inventors:

1. Abdalla Darwish, 67 Monterrey, Kenner, LA 70065
2. Sergey Sarkisov, 2305 Fleer Circle, Huntsville, AL 35803

Place of performance:

2305 Fleer Circle, Huntsville, AL 35803

Abstract:

A method and apparatus for pulsed laser deposition on composite films that use multiple high-power laser beams of different wavelengths and multiple targets in combination with the variable tilt of targets for achieving optimal overlapping between multiple plumes over the substrate, rastering of the beams over the targets, switching the targets between the beams and cooling the targets to a temperature as low as the temperature of liquid nitrogen that make possible to improve the uniformity and quality of polymer nano-composite coatings.

Description of the problem that motivated the invention:

A. General description of the problem

There is a great need for polymer nano-composite films selectively deposited on small areas of different substrates. Applications vary from miniature chemical and biosensors, light emitters, detectors of e-m radiation from IR to gamma, etc. Unique features of the pulsed laser deposition (PLD), such as control of film thickness with good accuracy, uniform coating, good control of the film composition, capability of depositing films selectively in miniature (micron and submicron-size) areas make it very attractive as a tool for making polymer nano-composite films.

B. Key or unique problem characteristics

Currently pulsed laser deposition of polymer nano-composite films is usually conducted with a UV laser beam that is alternatively focused either on the polymer target or on the additive target (see, for instance, Schlenkrich, F., Seyffarth, S., Fuchs, B., Krebs, H.-U., "Pulsed laser deposition of polymer–metal nano-composites", Applied Surface Science 257 (2011) 5362–5365). This has the following deficiencies: (a) UV radiation has a tendency to disintegrate polymer molecules, so the resulting film consists mostly of the polymer fragments or even monomers and has degraded quality; (b) alternating deposition of the polymer followed by additives results in a film with poor mixing of the additives in the film (stratification). A number of methods have been proposed recently to overcome dissociation of polymers in PLD, such as the matrix assisted pulsed laser evaporation (MPLE) using UV, visible or near-IR radiation and the resonant IR (RIR) PLD with the IR radiation in resonance with the vibrational modes of the polymer molecules. As far as the polymer nano-composites are concerned, the latter methods have never been combined with PLD deposition of any additives. And, if they will be, the combination will be the old fashion alternating deposition resulting in the stratified distribution of the additives across the film thickness. Hence the tools would be desirable to overcome the deficiencies mentioned above.

C. Prior art

U.S. Patent No. 5,192,580 (3/9/1993) “Process for making thin polymer film by pulsed laser evaporation” teaches a process for producing thin film of a first addition polymer on a substrate comprising bombarding a target, consisting essentially of a second addition polymer, with radiation from a pulsed laser in a vacuum or gas atmosphere to form a plume of components of said second polymer; and depositing said plume on a substrate, whereby a film of said first polymer is formed. The first and second polymer may be identical or different and in both cases may be fluoropolymers, acrylic polymers, or polyethylenes.

U.S. Patent No. 5,304,406 (4/19/1994) “Method for forming an organic film” teaches a process, which comprises continuously conducting purification of the raw material and deposition of the film in the same apparatus. The object of the invention is to introduce at least once an intermediate step of sublimating and recrystallizing the raw material to thereby provide films of improved quality by reducing the impurity concentration thereof.

U.S. Patent No. 5,490,912 (2/13/1996) “Apparatus for laser assisted thin film deposition” teaches a pulsed laser deposition apparatus that uses fiber optics to deliver visible output beams. One or more optical fibers are coupled to one or more laser sources, and delivers visible output beams to a single chamber, to multiple targets in the chamber or to multiple chambers. The laser can run uninterrupted if one of the deposition chambers ceases to operate because other chambers can continue their laser deposition process. The laser source can be positioned at a remote location relative to the deposition chamber. The use of fiber optics permits multiplexing. A pulsed visible laser beam is directed at a generally non-perpendicular angle upon the target in the chamber, generating a plum of ions and energetic neutral species. A portion of the plume is deposited on a substrate as a thin film. A pulsed visible output beam with a high pulse repetition frequency is used. The high pulse repetition frequency is greater than 500 Hz, and more preferably, greater than about 1000 Hz.

U.S. Patent No. 5,711,810 (1/27/1998) “Apparatus for variable optical focusing for processing chambers” teaches a pulsed laser deposition system with the two optical actions of focusing and rastering, and the optical chamber window combined into a single optical system. The single optics system is mounted on the processing chamber. Combining the three separate optical functions into one optics system facilitates laser beam control and reduces the space needed for the apparatus.

U.S. Patent No. 5,747,120 (5/5/1998) “Laser ablated coating for microtools” teaches wear-resistant coatings composed of laser ablated hard carbon films that are deposited by pulsed laser ablation using visible light on instruments such as microscope tips and micro-surgical tools. Hard carbon known as diamond-like carbon films produced by pulsed laser ablation using visible light enhance the abrasion resistance, wear characteristics, and lifetime of small tools or instruments, such as small, sharp silicon tips used in atomic probe microscopy without significantly affecting the sharpness or size of the device. For example, a 10-20 nm layer of diamond-like carbon on a standard silicon atomic force microscopy tip enables the useful operating life of the tip to be increased by at least twofold. Moreover, the low inherent friction coefficient of the DLC coating leads to higher resolution for AFM tips operating in the contact mode.

U.S. Patent No. 6,025,036 (2/15/2000) “Method of producing a film coating by matrix assisted pulsed laser deposition” teaches a pulsed laser deposition method in which the material that forms the coating material is first combined with a matrix material to form a target. The target is then exposed to a source of laser energy to desorb the matrix material from the target and lift the coating material from the surface of the target. The target and the substrate are oriented with respect to each other so that the lifted coating material is deposited as a film upon said substrate. The matrix material is selected to have the property of being more volatile than the coating material and less likely than the coating material to adhere to the substrate. The matrix material is further selected as having property such that when the target is exposed to a source of laser energy, the matrix material desorbs from the target and lifts the coating material from the surface of the target. The matrix material can be a solvent of the polymer coating material frozen to form a solid target.

U.S. Patent No. 6,998,156 B2 (2/14/2006) “Deposition of thin films using an infrared laser” teaches the transfer of a solid target material onto a substrate by vaporizing the material by irradiating it with intense light of vibrational mode of the material and depositing the vaporized material on a substrate in a solid form.

U.S. Patent Application No. 2011/0111131 A1 (5/12/2011) “Method for producing a multicomponent, polymer- and metal-containing layer system, device and coated article” teaches a method for producing layer systems on substrates that includes irradiating a first vacuum coating source with an irradiating source. The first vacuum coating source includes a first layer material that is dissolved in a solvent. A second vacuum coating source is applied to the substrate via a chemical vapor deposition process. In the way, novel layer systems and mixed layers, in particular mixed layers of polymers and metals or metal oxides can be applied.

D. Disadvantages or limitations of prior art

The prior art has the following disadvantages:

1) Multiple laser beams of a variety of wavelengths cannot simultaneously be applied to separate targets to deposit a composite film on the same substrate. U.S. Patent No. 5,490,912 (2/13/1996) “Apparatus for laser assisted thin film deposition” has a provision for using multiple laser beams possible applied to different targets, but those beams must be of visible spectral range and relatively low power because they are delivered via optical fibers.
2) The angle of a target cannot be changed with respect to a laser beam in order to achieve the adjustment of the position and the angle of the corresponding plume with respect to the substrate and control the size of region over the substrate where multiple plumes overlap and deposit the composite film of a variable proportion between the components.
3) The variable angle of the target surface is not combined with target lateral motion (with respect to the laser beam) for rastering of its surface necessary to provide smooth and uniform deposition.

4) The target holder does not accommodate for multiple rotating target with variable angle in combination with the means of target cooling to the temperature as low as the temperature of liquid nitrogen suitable for the matrix assisted pulsed laser evaporation (MAPLE) of polymers and fabrication polymer-inorganic nano-composite films.

Description of the invention

A. Purpose of the invention

The purpose of the invention is to eliminate the deficiencies of the prior art, namely, (a) the lack of combining multiple plumes from different targets individually and simultaneously exposed to multiple laser beams of the wide variety of wavelengths that results in poor mixing of the additives in polymer nano-composite films; (b) lack of combining polymer friendly PLD methods, such as MAPLE and RIR PLD, with conventional UV PLD more suitable for inorganic additives; (c) lack of combining of the control of the target surface angle with target rotation and cooling the target for achieving overlapping of the plumes from different target and achieving superior quality of the polymer nano-composite film produced.

B. Identification of component parts of the system

The schematic diagram of the apparatus of the invention is presented in Fig. A1. The apparatus consists of multiple laser beams and targets. For the sake of simplicity, the case of only two laser beams 1 and 2 are considered. Beams 1 and 2 strike targets 3 and 4 respectively. Targets 3 and 4 are mounted on target holders 5 and 6 respectively. The said target holders are mounted on bases 7 and 8 respectively. The said bases are mounted on a cooling stage 9. The substrate stage 10 is placed in front of the said targets. The said laser beams strike the said targets and create plumes of their material 11 and 12 respectively that overlap in region 13 over deposited film 14 on substrates 15. The said cooling stage can rotate around its axis along direction 16 to facilitate switching the targets. Target holders 5 and 6 move in lateral directions 17 and 18 with respect to the corresponding laser beams to facilitate rastering and uniform exposure of the said targets to the said laser beams. Bases 7 and 8 tilt along directions 19 and 20 respectively to adjust overlapping region 3 between the said plumes. The apparatus is enclosed in a vacuum chamber (not shown) with optical windows (not shown) for the said laser beams. The beams are directed form laser sources (not shown) by a conventional beam guiding fixtures made of high-power optical mirrors (not shown). The said fixtures are equipped with beam shutters (not shown) that can block any particular laser beam form hitting the target. The beams are focused on the said targets with conventional focusing lens systems (not shown). The said vacuum chamber has entries (not shown) for several carrier gases to be used in the PLD process.

C. Method

The method consists of the following steps:

1) Targets are pre-cooled and preserved in solid state.
2) Targets 3 and 4 and substrate 15 are mounted on their holders.
3) Vacuum is created in the vacuum chamber and a carrier gas is fed in.
4) The targets are exposed to the corresponding laser beams.

5) Bases 7 and 8 are tilted in order to obtain a desirable overlapping region 13 between plumes 11 and 12.
6) The PLD process is conducted until film 14 of a desirable thickness is obtained on substrates 15.
7) The said laser beams can be kept simultaneously on sequentionally shut down the composite film 14 of a different mixture of the components and their location across the thickness of the film.
8) The said laser beams can be attenuated to achieve different proportions of the components in the composite film.
9) Bases 7 and 8 can be tilted along directions 19 and 20 respectively in order to achieve the optimal overlapping region 13 of plumes 11 and 12 over substrate 15.
10) Stage 9 can be rotated along direction 16 around it axis to switch the targets between the beams.
11) Target holders 5 and 6 can move along directions 17 and 18 lateral to the respective beams in order to achieve rastering and uniform consumption of the target materials.

D. Alternate embodiments

In one alternative embodiment target 3 can be made of solid polymer, such as poly(methyl methacrylate) known as PMMA and target 4 made of metal, such as gold. Laser beams 1 and 2 can be of the same wavelength, such as 1064 nm (the fundamental harmonic of an Nd:YAG laser) or can have different wavelengths: 255 nm (the 4-th, UV harmonic of the Nd:YAG laser) for the said polymer target 3 and 532 (the 2-nd, visible harmonic of the Nd:YAG laser) for metal target 4.

In yet another alternative embodiment the said target 3 is made of polymer PMMA dissolved in as solvent, such as toluene or chlorobenzene, and frozen to a solid state in liquid nitrogen. Then the said target is mounted on cooling stage 9 continuously cooled with circulating liquid nitrogen. Then the said target is exposed to the UV laser beam to implement the matrix assisted pulsed laser evaporation (MAPLE) process in which the frozen solvent dissipates the energy of the UV laser into heat transferred to the polymer that evaporates without dissociation and condensates on substrate 15 together with the material from the second target 4 to form a polymer nano-composite film 14.

In yet another alternative embodiment the number of targets and laser beams of different wavelengths are more than two to implement PLD of multi-composite films.

In yet another alternative embodiment the laser wavelength is chosen to be in the mid-IR, namely in resonance with the frequency of the vibrational modes of the polymer molecules of the polymer target 2 to implement the resonance IR (RIR) PLD of polymer nano-composites, which does not cause dissociation of the deposited polymer material.

In yet another alternative embodiment the laser wavelength is chosen to be in the mid-IR, namely in resonance with the frequency of the vibrational modes of the molecules of the frozen solvent matrix of the frozen polymer-solvent target 2 to implement the resonance RIR MAPLE of polymer nano-composites, which the most gentle laser deposition process suitable for highly sensitive polymer molecules, such as proteins or DNAs.

Unique or novel features of the innovation and the results or benefits of its application

A. Novel and unique features

The apparatus has provisions for and the method uses:

1) Multiple high-power pulsed laser beams of a variety of wavelengths that can be simultaneously applied to separate targets to deposit a composite film on the same substrate.
2) Variable angle of each target with respect to its laser beam in order to achieve the adjustment of the position and the angle of the corresponding plume with respect to the substrate in order optimize the size of region over the substrate where multiple plumes overlap and deposit the composite film of a variable proportion between the components.
3) Combination of the variable angle of the target surface with target lateral motion (with respect to the laser beam) for rastering of its surface necessary to provide smooth and uniform deposition.
4) A rotating target stage for switching targets between different laser beams.
5) The target stage combined with the means of target cooling to the temperature as low as the temperature of liquid nitrogen suitable for MAPLE and RIR MAPLE processes.

B. Advantages

The apparatus and the method make possible to

1. Create polymer nano-composite films of more uniform mixture of the components because they are simultaneously deposited on the substrate form multiple targets hit by multiple laser beams.
2. Create polymer nano-composite films of more uniform thickness and distribution of the components along the film duet to optimized overlapping of the plumes from multiple targets achieved by the variation of the tilt of each target with respect to its laser beam.
3. Improve the uniformity of the film also due to combination of the lateral motion of the target with respect to its laser beam to achieve rastering and uniform consumption of the target material.
4. Achieve better quality of the polymer (less proportion of monomers and polymer fragments) coating due to the use of MAPLE or RIR MAPLE techniques provided by the cooling stage.
5. Dramatically widen the variety of the produced coating by switching the said targets between different laser beams with the use of the rotary target stage.

C. New concept

The method uses a new concept of variable tilt of the said target in order to change the position of the plume with respect to the substrate and optimize the overlapping between the plumes of different targets.

In the prior art PLD produces pretty much one thin film over the other and one material at a time. So, it is either single layer of one material, or multiple layers of the same or different materials.

This makes impossible to reproduce a process similar to the growth of an evenly doped crystal. In a conventional crystal growth process either from a solution or melt, when the crystal is intended to be evenly doped, for instance, with transitional metal ions, the dopants take evenly places of the main ions, or interstitial sites during the growth since both materials grow at the same time in situ. So, the need to fabricate a PLD thin film analogous to an evenly doped crystal has never been met before. The proposed method and apparatus uses at least two different beams at the same time to ablate two different materials in situ, not one after another or to alternate between targets for the same laser beam (this will give one film at a time). Therefore, having at least two beams instead of one allows the interaction between different species, adds the ability to control the proportion of the dopant material added and give the lets dopant ions to migrate and settle in their position in the crystal. This will provide am accurate control of the process to tailor the properties of doped thin film in a desirable way. The overlap of at least two plumes, will be achieved with the tilt of the target holders (never been done before for two-beam PLD in situ).

Speculations regarding potential commercial applications and points of contact

The apparatus and method can be used in commercial applications using polymer nano-composite coatings, such as (a) chemical and bio-sensors (polymers doped with indicator dyes and metal nano-particles for chemical sensing or polymers doped with antibodies and nano-particles for bio-sensing); (b) fluorescent coatings and scintillation radiation sensors (polymers doped with nano-particles of the oxides and salts of the rare earth elements) and others. The invention is of great interest to the petro-chemical industry (using sensors of hazardous chemical species), food and agriculture industries (using sensors of hazardous bio-species); nuclear power industry (miniature sensors of harmful radiation); home land security and defense (detectors of weapons of mass destruction, “dirty bombs”, and improvised explosives) and others.

Points of contact of the potential users:

1. U.S. Naval Research Laboratory, Washington, D.C. 20375-5345; Dr. Douglas B. Chrisey, Head, Plasma Processing Section, Naval Research Laboratory.
2. AFRL - Materials and Manufacturing Directorate, AFRL/RX, Building 653, 2977 Hobson Way, Wright-Patterson AFB, OH 45433-7734, Website: http://www.wpafb.af.mil/afrl/rx/, Technology Transfer Website: http://www.wpafb.af.mil/library/factsheets/factsheet.asp?id=6026, Agency/Department: Dept. of Defense - Air Force, Region: Midwest. FLC Laboratory Representative**:** Mr. Greg McGath, Phone: 937-255-5669, Fax: 937-656-4831, Email: Gregory.McGath@wpafb.af.mil.

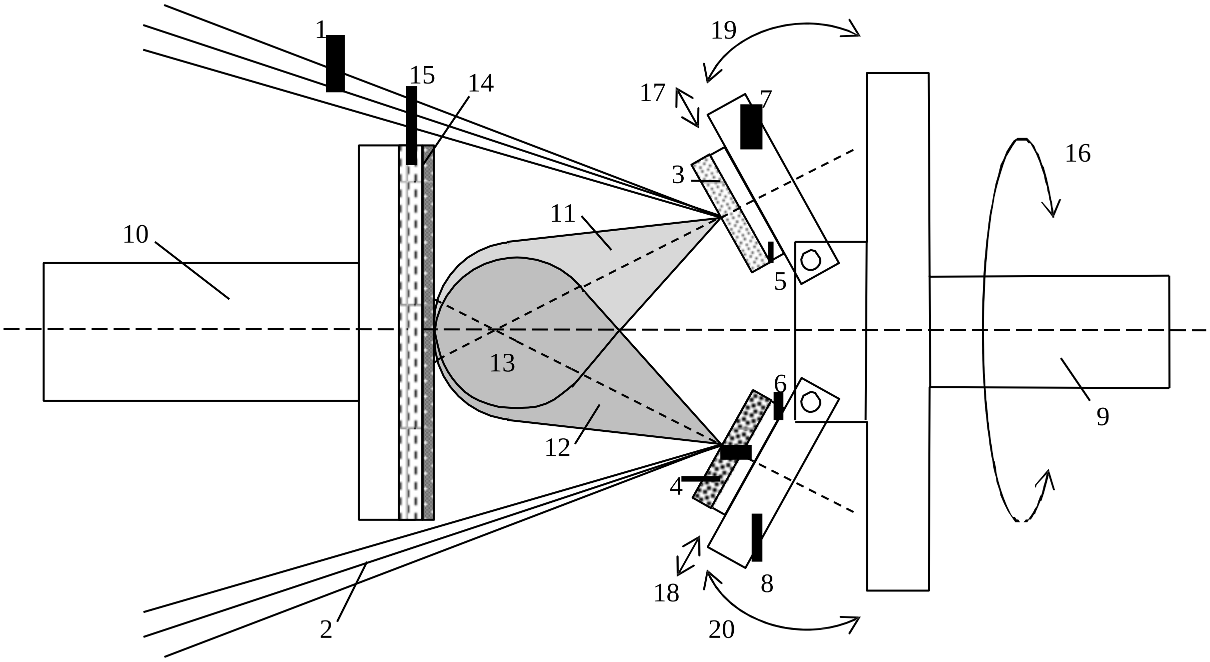

Figure A1

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
61/850,330	02/14/2013		125			

CONFIRMATION NO. 8727

Sergey Sarkisov
2305 Fleer Circle
Hunstville, AL 35816

FILING RECEIPT

OC000000059754439

Date Mailed: 03/13/2013

Receipt is acknowledged of this provisional patent application. It will not be examined for patentability and will become abandoned not later than twelve months after its filing date. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections

Inventor(s)

Abdalla Darwish, Kenner, LA;
Sergey Sarkisov, Hunstville, AL;

Applicant(s)

Abdalla Darwish, Kenner, LA;
Sergey Sarkisov, Hunstville, AL;

Power of Attorney: None

If Required, Foreign Filing License Granted: 03/08/2013

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is US 61/850,330

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No
** SMALL ENTITY **
Title

Method and apparatus for multi-beam pulsed laser deposition of thin films

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Absorption-fluorescence spectrometer AFS-PNC-X

The project is concern about pushing the envelope of the characteristic of the polymers beyond its limitation and introduce new practical materials which can do more in the next level of the material characteristics and tailoring the polymeric materials to for new set of application as a test of the characteristic of the new materials . For that, the Absorption-fluorescence spectrometer AFS-PNC-X from SSS Optical Technologies was acquired in order to evaluate performance of the fabricated polymer nanocomposite films as chemical gas sensors and light emitters as a test. The spectrometer is a customized system, which has a gas inlet and outlet, visible (610 nm) LED source and a supplemental infra-red 980-nm laser diode (for the studies of the upconversion fluorescence). The basic package includes: sample holder SH-1; readout/power module with laptop computer (with the LabVIEW software pre-loaded) and data acquisition module; junction box; cable; gas adapter; gas cylinder; pressure regulator; Tygon tubing, 3/16” ID (4 ‘); manual; and spare kit. Figs. 1 through 5 show the installation diagram, the sample holder connected to the junction box, the readout/power module, the gas adapter with the gas cylinder and the pressure gauge, and the sample holder connected to the gas adapter.

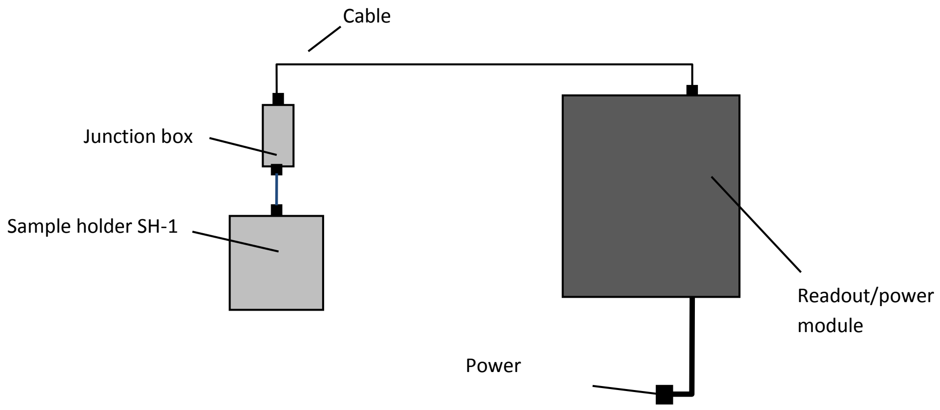


Figure 1. Installation diagram.

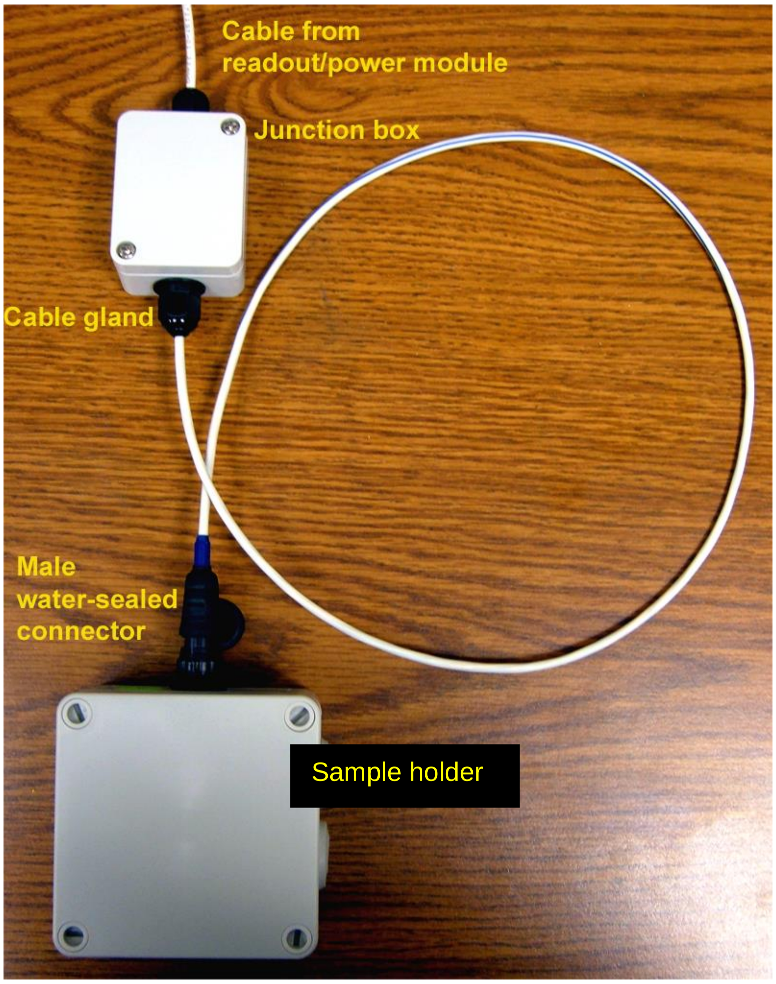


Figure 2. Sample holder SH-1 connected to junction box.

Figure 3. Readout/power module with cables connected.

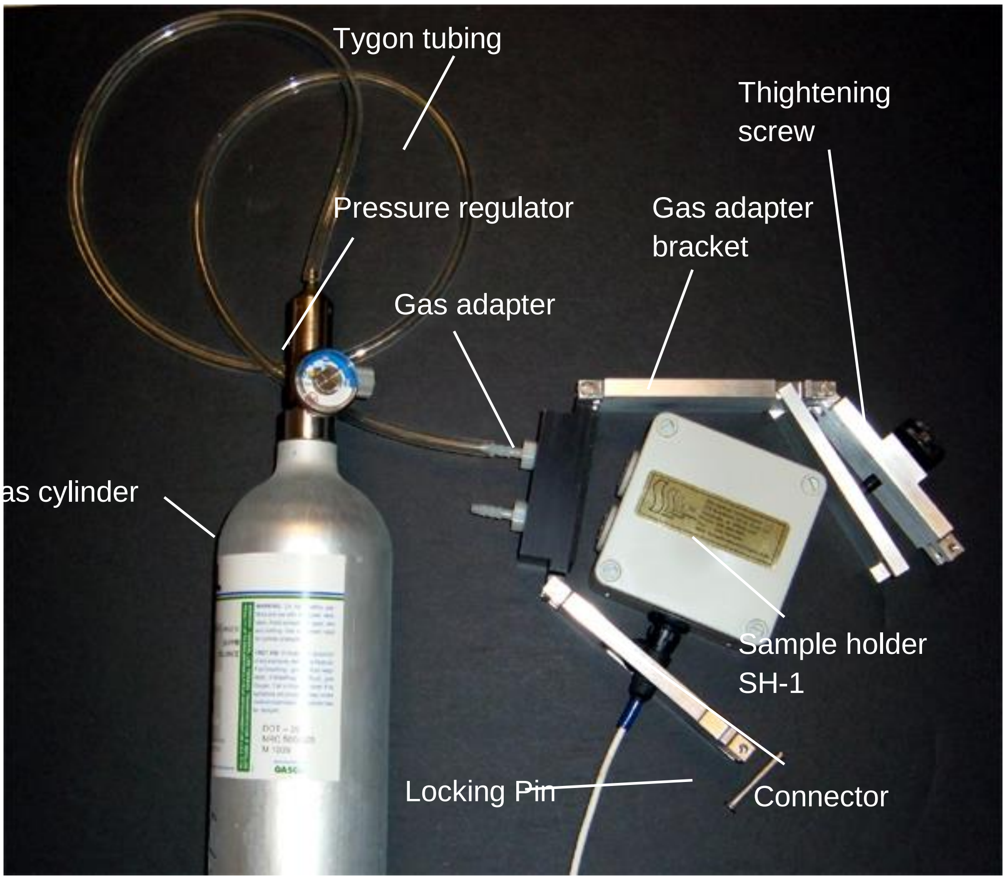


Figure 4. Sample holder SH-1 shown with the gas cylinder connected to the gas adapter and the gas adapter disengaged.

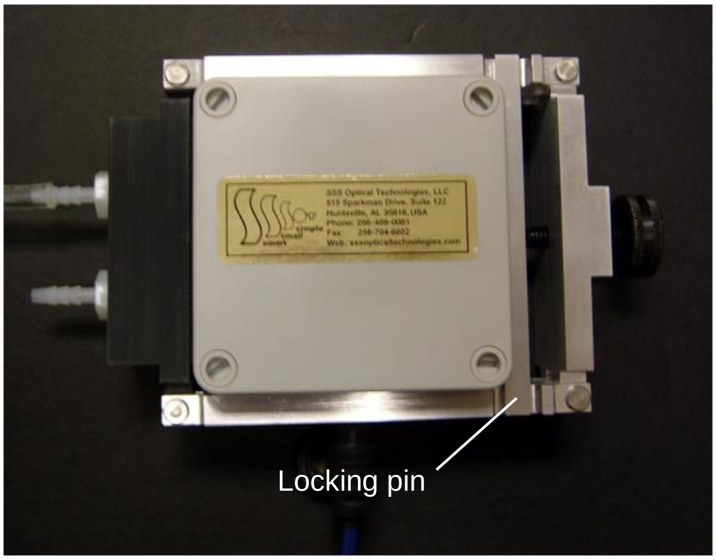


Figure 5. Sample holder SH-1 with the gas adapter fully engaged.

The instrument has been used to evaluate gas sensing properties of the polymer nanocomposite films made from polymers poly(methyl methacrylate) (PMMA) and polymiimide, nanoparticles of gold, and an indicator dye, such as bromocresol purple (BCP). The experiments were conducted to evaluate the response of the films to ammonia, hazardous air pollutant.

The example of the differential optical absorption spectra between the polyimide film (with BCP added) doped with gold nano-particles and the reagent without nano-particles is presented in Fig. 6. The reagent with nano-particles under exposure to ammonia at a concentration of ~ 10000 ppm transmitted 100 times less light on both sides of the 605-nm peak and 31 times less - near the peak. The expansion of the absorption band in both directions relative to the 605-nm peak was more likely due to the LSPR in strongly aggregated gold nano-particles (compare with line 4 in Fig. 6 – the optical extinction spectrum of the aggregated Au nano-colloid). Therefore, a light beam incident at an angle of ~ 90o and making just a single pass across a layer of the new, nano-colloid enhanced reagent material exposed to ammonia would experience the drop of the intensity equivalent to that of the beam passing along a roughly 100 times thicker old reagent material exposed to the same concentration of ammonia.

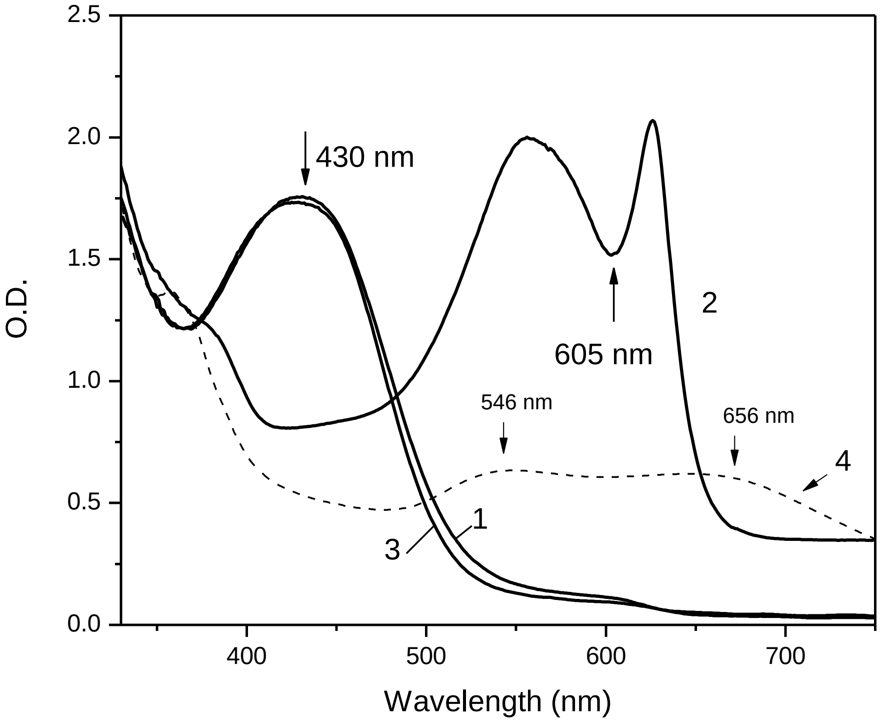


Figure 6. Differential optical absorption spectra between the nanocomposite polyimide film doped with gold nano-particles and the film without nano-particles. Curve 1 corresponds to the case when both samples (previously exposed to ammonia numerous times) stayed in air without ammonia; 2 – samples exposed to the same amount of ammonia (~ 10000-ppm concentration) until the absorption was saturated; 3 – at > 3 h after ammonia is removed. Curve 4 is the optical extinction spectrum of the aggregated Au nano-colloid in GBL used for preparing the reagent film. O.D. stands for Optical Density = – [Log(Transmittance)].

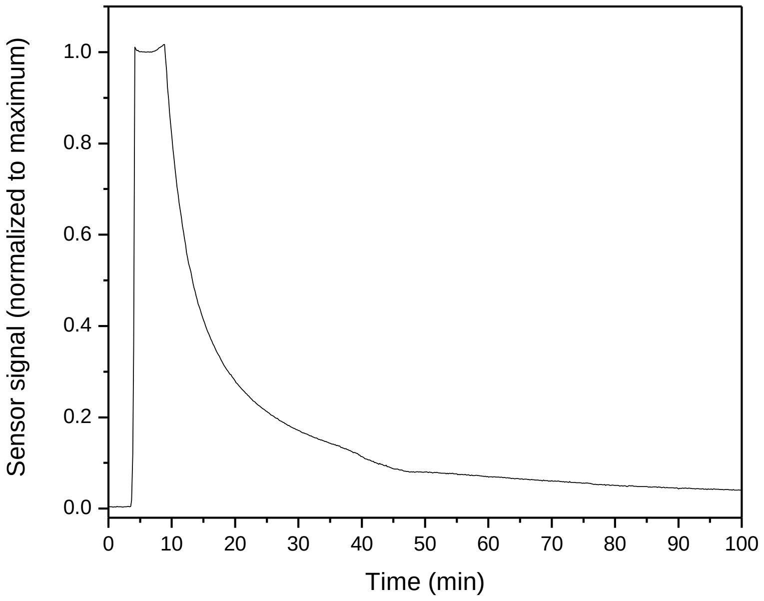
The response time of the nanocomposite film was determined by exposing it to a standard mixture of ammonia in dry air at a minimal flow rate of 10 mL/min, The interrogation method is based on the reading of the drop of the light from the light emitter (orange LED in the sample holder SH-1) passing through the reagent film exposed to ammonia (inside SH-1) in the photodetector (also inside SH-1) acquired and processes with the readout/power module of spectrometer AFS-PNC-X. Fig. 7a illustrates a typical response of the nanocomposite film to the ammonia mixture in air at a concentration of ~ 74.3 ppm. The plateau in the response signal corresponds to the equilibrium reached between the competing processes the ammonia diffusion in and out of the film. During the calibration of the response, the film was exposed to different concentrations ranging from zero to 100 ppm with slightly shorter response time for smaller concentrations. Typical calibration plot for the film as an ammonia sensor is presented in Fig. 4b. The output signal at 100 ppm corresponded to ~ 15-20 % drop of the optical transmittance of the reagent layer. One of the advantages of the nanocomposite film was that the exposure to the ammonia much greater concentrations (> 10000 ppm) did not cause any damage and the film was able to fully recover. The potential optimal use of the nanocompmposite film would be for monitoring one-hour Time-Weighted Average (TWA) levels of ammonia.

Conclusions of the nanocomposite material testing

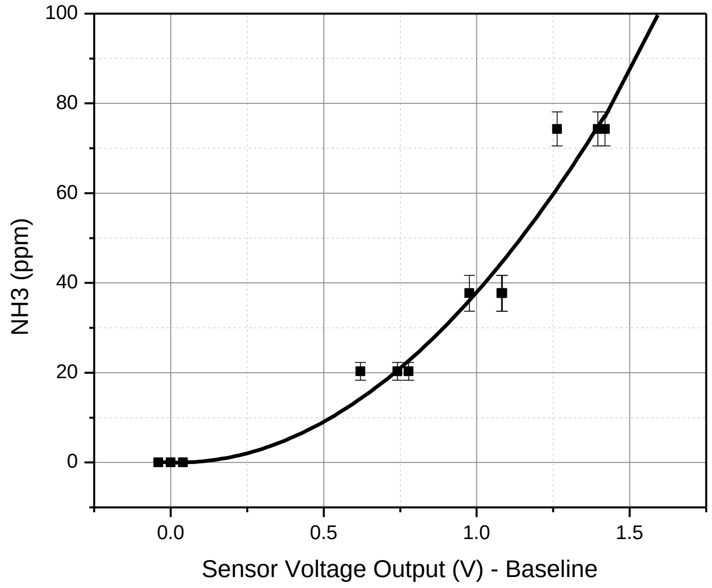
Spectrometer AFS-PNC-X has been successfully used to evaluate the response of the polymer nanocomposite films to ammonia. The experimental data indicate that the films can be used as the sensors monitoring one-hour Time-Weighted Average (TWA) levels of ammonia within the range 1 to 100 ppm. They can fully recover after prolonged exposures to much higher levels of near 10000 ppm. The research paper discussing these findings is in the process of preparation.

Future plans to use the instrument

In case the instrumentation proposal submitted in response to the DoD HBCU Instrumentation Program Fy2014 will be funded, spectrometer AFS-PNC-X will be integrated with Analyzer AOR-002 from SSS Optical technologies, LLC. The readout/power module of AFS-PNC-X will be used to measure the optical response of the (multi-beam pulsed laser deposition) MPLD made thin nanocomposite films to various gases in order to evaluate their efficiency as chemical sensing agents. The gases to be used include ammonia, oxygen, and hydrogen. The diluting gas will be nitrogen. The response will be evaluated at sub-atmospheric and low (< 1 Torr) pressure. Analyzer AOR-002 will use at least one laser source, such as 980-nm near-IR laser, to initiate upconversion fluorescence of the MPLD prepared polymer nanocomposite films doped with nanoparticles of the upconversion phosphors. At least two photodetectors will be used to measure the intensity of transmitted and upconversion fluorescence light and evaluate the response of the films to exposure to the target gases.



(a)



(b)

Figure 7. (a) Response of the nanocomposite polyimode-BCP/gold film to 74.3 ppm ammonia (in air) at a flow rate of ~ 10 mL/min; rise time was 0.6 min (from zero to 90% maximum), fall time – 33 min (from maximum to 10% maximum after the exposure is stopped). (b) Typical calibration plot of the ammonia sensitive film. Baseline = 1.155 V. (b)