Multi-beam pulsed laser deposition: new method of making nanocomposite coatings

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ABSTRACT

Huge number of new photonic devices, including light emitters, chemical sensors, and energy harvesters, etc. can be made of the nanocomposite coatings produced by the new multi-beam pulsed laser deposition (MB-PLD) process. We provide a short review of the conventional single-beam PLD method and explain why it is poorly suitable for making nanocomposite coatings. Then we describe the new MB-PLD process and system, particularly the multiple-beam matrix assisted pulsed laser evaporation (MB-MAPLE) version with laser beam scanning and plume direction control. The latter one is particularly designed to make organic (polymer) - inorganic functionalized nanocomposite coatings. Polymer film serves as a host for inorganic nanoparticles that add a specific functionality to the film. We analyze the properties of such coatings using the examples of poly(methyl methacrylate) (PMMA) films impregnated with the nanoparticles of rare-earth (RE) upconversion phosphors. They demonstrated the preservation of microcrystalline structure and bright upconversion emission in visible region of the phosphor nanoparticles after they were transferred in the polymer matrix during the MB-MAPLE process. The proposed technology has thus proven to serve its purpose: to make functionalized polymer nanocomposite coatings for a various potential applications.

Keywords: Multi-beam pulsed laser deposition, matrix assisted laser evaporation, upconversion light emitters, polymer-inorganic nanocomposite films, nanocomposite coatings

1. INTRODUCTION

Applying nanomaterials with specific functions to thin films is one of popular approaches to achieving multifunctional nanocomposite materials. Pulsed laser deposition (PLD) of nanocomposite films is a technology that allows to precisely control the thickness of the film and impregnate it with a variety of nanomaterials.[1,2] PLD is flexible; makes easy to implement film growth in any environment; provides exact transfer of complicated materials; provides variable growth rate; makes possible epitaxy at low temperature; makes possible resonant interactions (i.e., plasmons in metals, absorption peaks in dielectrics and semiconductors); atoms arrive in bunches, allowing for much more controlled deposition; greater control of growth (by varying laser parameters). However, the conventional single-beam approach (when at a given moment of time a single laser beam was used to deposit either a host material or a nanomaterial on the same substrate) resulted in non-uniform mixing (stratified distribution) of the nanomaterial in the host; poor control of the interaction of the components in the nanocomposite material; also different targets "like" different laser beams. These problems can be solved with the multi-beam (and multi-target) PLD (MB-PLD) with the host material and nanomaterial being deposited concurrently.[3-5] For instance, in the double-beam version of MB-PLD (DB-PLD) two materials are ablated by two laser beams simultaneously; the ejected materials form plasma plumes and expand across to the substrate where they are deposited as a film; and the more uniform composite films can be made This paper discusses further improvements of MB-PLD based on optimal handling of more gentle polymer targets for making polymer nanocomposite films and optimal control of the directions of the plumes emanating from several targets.

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2. MATERIALS AND METHODS

2.1. Multi-beam pulsed laser evaporation

The conventional single-beam PLD of a single material on a substrate includes the sequence of the following processes: (a) heating a single target with a pulsed laser beam; (b) melting the heated target material followed by its vaporization; (c) ionizing the atoms of the vaporized target material by the electrons accelerated in the strong electric field of the laser beam and creating weakly ionized plasma; (d) expansion of the plume made of the weakly ionized plasma driven by electrostatic repulsion of the positive ions of the target material towards the ambient gas or vacuum separating the target from the substrate; (e) condensation of the target material from the plume on the substrate and thin film formation. Since the spread of the plume is driven by electrostatic repulsion, the axis of the plume is always normal to the surface of the target regardless of the direction of the incident laser beam.

The idea of using pulsed laser beams for deposition of polymer films has been met with skepticism more than three decades ago, when the technology was conceived. The reason was the fear that a high energy laser pulse breaks up a “tender” polymer molecule into fragments before it gets from the target on the substrate. Despite initial skepticism, laser assisted deposition of polymers, thanks to technological advances, has gained popularity in recent years. One of the popular “gentle” variations of PLD in terms of handling polymer targets is the matrix assisted pulsed laser evaporation (MAPLE).[3-5] In MAPLE, a frozen matrix consisting of a dilute solution (1-5%) of a polymer in a relatively volatile solvent is used as the laser target. The solvent and concentration are selected so that first, the material of interest can dissolve to form a dilute, particulate free solution, second, the majority of the laser energy is initially absorbed by the solvent molecules and not by the solute molecules, and third, there is no photochemical reaction between solvent and the solute. The light-material interaction in MAPLE can be described as a photothermal process. The photon energy absorbed by the solvent is converted to thermal energy that causes the polymer to be heated but the solvent to vaporize. As the surface solvent molecules are evaporated into the gas phase, polymer molecules are exposed at the gas-target matrix interface. The polymer molecules attain sufficient kinetic energy through collective collisions with the evaporating solvent molecules, to be transferred into the gas phase. By careful optimization of the MAPLE deposition conditions (laser wavelength, repetition rate, solvent type, concentration, temperature, and background gas and gas pressure), this process can occur without any significant polymer decomposition. The MAPLE process proceeds layer-by-layer, depleting the target of solvent and polymer in the same concentration as the starting matrix. When a substrate is positioned directly in the path of the plume, a coating starts to form from the evaporated polymer molecules, while the volatile solvent molecules are evacuated by the pump in the deposition chamber.

Mixing the components of different nature, organic polymers and inorganic dopants, in the same target at a certain proportion and exposing them to the same laser beam not necessarily can result in good quality composite films. The laser pulse energy and wavelength is not optimized for each component individually and the mixing proportion in the composite film is dictated by the initial proportion of the target and thus cannot be changed in the process. These limitations can be removed in the method of multi-beam deposition using several separate targets, such as MAPLE polymer target 1, inorganic target 2, etc. each being simultaneously ablated by a separate laser beam of different wavelength.[3-5] This method can be loosely called the multi-beam MAPLE or MB-MAPLE. A three-beam MB-MAPLE system has been recently built at Dillard University.[6] MAPLE polymer target 1 is frozen (to a temperature of liquid nitrogen) and ablated by a 1064 nm laser beam from a Q-switched Nd:YAG pulsed laser. The inorganic PLD target 2 in the form of solid pellet is ablated by the 532-nm frequency doubled beam from the same laser. Oscillating bema reflectors mounted on the system provide continuous scanning of the beams over the targets in order to prevent premature target cracking due to caters resulting from the ablation in a single spot. The system also exploits the plume direction control that stabilizes overlapping of the plumes form different targets on the substrate. This secures the uniformity of the deposited nanocomposite film.

2.2. Plume direction control

Fig. 1 depicts the flow chart of the algorithm of for the feedback control of the target tilt angle. The process starts by selecting a still image of the plume or plumes taken with attached video camera. The image may be one of many, or a single image delayed from a laser pulse. If the image is in color, the color may be converted to gray scale, for example, by selecting or summing one or more color signals. Camera scale or linearity corrections may also be made. A meaningful portion of the image is selected for detailed processing to reduce processing time. The image is then binarized, i.e., the brightest portion of the plume is identified by thresholding the intensity values. Pixels brighter than a predetermined threshold are set to “1” and those less than the threshold are set to “0”. The image is further binarized to define an outline by setting the “1” pixels with a “0” neighbor to “1” and the remaining pixels to “0”. The next step is to process the plume image to determine the principle axis as previously described. The desired point of intersection of the axis on the substrate is then identified. If the plume axis meets the desired location, the process repeats with another laser pulse. If not, the feedback is adjusted to tilt the target to correct the axis deviation.

Fig. 2 shows the diagram explaining further details of the feedback process. The laser trigger initiates a laser pulse. A video camera is directed to view a desired portion of the plume. The laser trigger is also used to synchronize the camera timing with respect to the laser pulse and obtain an image after desired development of the plume. The selected image is then processed for color or scale correction to produce a gray scale (intensity) image. The gray scale image is then processed to obtain plume direction information. Plume direction may be derived from plume shape or position. Plume shape may be determined by thresholding the intensity information. Plume position may also be determined by thresholding and determining the centroid or other feature relative to the laser spot on the target. A measured plume axis is determined as the longest length of the determined shape (or may be determined as the position of a plume feature: for example, centroid or peak) relative to the plume origin at the laser spot on the target. A desired axis direction is predetermined based on desired deposition, for example the center of the substrate. The measured plume axis direction is then compared with the desired plume axis direction to generate a plume axis direction error signal. The error signal is filtered to reduce noise. The filtered error signal is used to develop a control signal that is fed to the tilt servo and linkage to adjust the target platform angle and thus adjust the plume angle.

2.3. Multi-beam deposition with switchable targets

Fig. 3 presents the configuration of the multi-beam deposition system with multiple switchable targets mounted on rotary holders. The system has two rotary holders with eight targets each. The system includes stepper motor 1 of rotary target holder (turret) 1, which does not tilt, and also stepper motor 2 mounted on a tilting platform. The two holders (turrets) are controlled by a controller driven by a processor. Each target holed (turret) has eight targets, but any number of targets may be placed as desired. The target materials may be the same, or different, as needed for the deposition. The multi-beam laser deposition system has at least two laser beams with about 10 levels of fluence in order to select different target ablation rates and thus different mixing rates between two simultaneously deposited target materials. The “laser off” mode can be considered as the “idle” ablation rate (no target material being deposited). With the turret for each laser beam having 8 targets, the total number of possible variations of the compound mixtures in the resulting composite film is equal to $(10x8+1)x(10x8+1) = (10x8+1)^2 = 81^2= 6561$. With three laser beams and three target holders respectively, the number of possible variations would be $81^3 = 531441$. Such arrangement dramatically increases the number of choices in the composition of the deposited film and its desired properties.

2.4. Multi-beam deposition with substrate manipulation

Fig. 4 presents an exemplary schematic of a variation of a six-degree-of-freedom substrate manipulation system. The exemplary shape of the said substrate is that of a hexagonal prism. The system consists of holder 2501 of substrate 118; the holder driven by a computerized translation/rotation actuator (not shown) moves the said substrate along three translational directions 2502 and three rotational directions 2503. The movements of substrate can be implemented in intermissions between the pulsed laser depositions in order to switch between the faces to be coated. The movements can be also implemented during the positions in order to change the angle of a particular face to be coated with respect to plumes 114 and 116 or to gradually change the thickness of a coating along a particular face. Combining substrate manipulation with target switching makes possible to coat different faces of the substrate with different composite coatings. An exemplary “substrate” 118 can be the steel blade of a knife. The blade is manipulated in such a way that its sharp edge is PLD coated with diamond coating enhancing its cutting capability. Then the blade can be turned to put one of its sides at a time in front of plumes 114 and 116 to deposit a nanocomposite film of polymer Teflon® doped with inorganic pigment nanoparticles to enhance the blade’s capability of sliding through a material and improve its esthetic appearance.

2.5. Resonant infrared pulsed laser deposition

The third channel of the multi-beam PLD system at Dillard University has been designed for resonant infrared pulsed laser deposition (RIR-PLD). RIR-PLD is a variant of conventional PLD in which the laser is tuned to vibrational modes in the target material. The intense laser irradiation is used to promote the solid phase material to a highly vibrationally excited gas-phase species in the ground electronic state that can be collected on a nearby substrate as a thin film. In the absence of electronic excitation, the complex chemical and physical structure of the organic material is preserved. So far, this approach has been used with polymers in the mid-infrared wavelength range (2-10 µm). Typical chemical bonds and their vibrational modes that have been utilized in RIR-PLD are O-H stretch (vibrational mode wavelength 2.90 µm), C-H stretch (vibrational modes 3.28, 3.30, 3.38, 3.40, 3.42, and 3.45 µm), and C-O stretch (8.96 µm). One variation uses a MAPLE target in the form of emulsion of solvent and ice. RIR-MAPLE used laser radiation at a 2.94 nm in strong resonance with vibrational mode of the hydroxyl O-H bonds in the ice component of the emulsion matrix. In this way, the types of materials that can be deposited using RIR-MAPLE have been significantly expanded. Furthermore, materials with different solvent bond energies can be co-deposited without concern for material degradation and without the need to specifically tune the laser energy to each material solvent bond energy, thereby facilitating the realization of organic/inorganic hybrid nanocomposite thin-films.

Laser beam 3 (for RIR-PLD or RIR-MAPLE) is generated by a pulsed optical parametric oscillator source (OPO). The OPO is a laser pumped resonant cavity containing a nonlinear optical element (crystal). The OPO converts an input laser wave (called "pump") with frequency ω_p into two output waves of lower frequency by means of the second-order nonlinear optical interaction. The two output waves are called "signal" with frequency ω_s and "idler" with frequency ω_i, where signal is the output wave with higher frequency $\omega_s > \omega_i$. The sum of the output waves' frequencies is equal to the pump wave frequency $\omega_p = \omega_s + \omega_i$. An advantage of the OPO is that the output wave is tunable, and the range may be configured to cover the one to three micron range, where polymer and solvent resonances are typically found. Typical chemical bonds and their vibrational modes that can be utilized are O-H stretch (vibrational mode wavelength 2.90 µm), C-H stretch (vibrational modes 3.28, 3.30, 3.38, 3.40, 3.42, and 3.45 µm), and C-O stretch (8.96 µm). Thus the system may be operated in RIR or RIR-MAPLE operating modes. A particular resonance of the target material may be selected. The excitation may be preferentially directed to the polymer or an organic material (RIR mode) or to the solvent (RIR-MAPLE), if each has a separate absorption band, or may alternate between polymer and solvent (combined RIR/RIR-MAPLE mode) to find the conditions that yield the best quality deposition. The system uses OPO versaScan-ULD from GWU-Lasertechnik (Erftstadt, Germany) with non-linear crystal β-BaB2O4 (BBO) and the tuning ranges 400 to 709 nm for signal and 710 to 3500 nm (2857 cm^{-1}) for idler. It is pumped with the third harmonic (355 nm) of the Q-switched Nd:YAG pulsed laser Quanta-Ray Lab-170-10 from Spectra Physics (division of Newport, Newport, CA, USA). The pulse width of the pump laser beam is 2-3 ns, pulse repetition rate is 10 Hz, and energy per pulse is 220 mJ. With the tuning range for the idler reaching 3.5 µm or 2857 cm^{-1}, the OPO can selectively deliver energy to the stretch mode O-H (2.9 µm) and C-H stretch modes (3.28, 3.30 µm).

Fig. 5 shows the IR absorption spectrum of the PMMA. It can be seen that there is a distinct absorption band from 1150 cm^{-1} to 1250 cm^{-1}, which can be attributed to the C–O–C stretching vibration. The two bands at 1388 cm^{-1} and 754 cm^{-1} can be attributed to the α-methyl group vibrations. The band at 987 cm^{-1} is the characteristic absorption vibration of PMMA, together with the bands at 1062 cm^{-1} and 843 cm^{-1}. The band at 1732 cm^{-1} shows the presence of the acrylate carboxyl group. The band at 1444 cm^{-1} can be attributed to the bending vibration of the C–H bonds of the $–CH_3$ group. The two bands at 2997 cm^{-1} and 2952 cm^{-1} can be assigned to the C–H bond stretching vibrations of the $–CH_3$ and $–CH_2$- groups, respectively. Furthermore, there are two weak absorption bands at 3437 cm^{-1} and 1641 cm^{-1}, which can be attributed to the –OH group stretching and bending vibrations, respectively, of the absorbed moisture. The tunable OPO can resonantly excite the C-H bond absorption bands at 2997 cm^{-1} and 2952 cm^{-1} and the –OH band at 3437 cm^{-1} and deliver energy to the PMMA molecules to heat them up and evaporate thus implementing the RIR deposition method. Figs. 6 a and b show the infra-red absorption spectra of chlorobenzene (Fig. 6a) and toluene (Fig. 6b) that are used do dissolve PMMA and prepare frozen (with liquid nitrogen) targets for the MAPLE. The tunable OPO can be used to resonantly excite vibrational bands between 3200 and 2900 cm^{-1} thus implementing the RIR-MAPLE method.

2.6. MB-MAPLE deposition of polymer nanocomposite films

In order to investigate the performance of the MB-MAPLE system at Dillard University, exemplary thin nanocomposite film upconversion emitters were deposited using the following procedure. A sample of the solution of poly(methyl methacrylate) known as PMMA in chlorobenzene at a proportion of 1.0 g solids per 10 mL liquids was poured in a copper cup of the MAPLE target holder and frozen in liquid nitrogen. Then the copper cup with the frozen polymer solution was installed in the vacuum chamber. Target 2 was made of a solid pellet prepared by compressing the powder of an upconversion phosphor ($NaYF_4$: Yb^{3+}, Er^{3+}; or $NaYF_4$: Yb^{3+}, Ho^{3+}; or $NaYF_4$: Yb^{3+}, Tm^{3+}) and retained in the second, small target holder. The laser source was a Spectra Physics Quanta Ray Nd:YAG Q-switched Lab-170-10 laser with a pulse repetition rate of 10 Hz, 850-mJ energy per pulse at the 1064-nm fundamental wavelength and 450-mJ energy per pulse at the 532-nm second harmonic. The targets were exposed to the fluences ranging from 0.053 J/cm^2 to

0.84 J/cm^2. Frozen polymer Target 1 was ablated with the 1064-nm laser beam. Target 2 was concurrently ablated with the 532-nm frequency doubled Nd:YAG beam. The fluences were adjusted to control the proportion of the upconversion material coming in the polymer at approximately 5% by weight.

3. RESULTS AND DISCUSSION

Fig. 7 presents the photograph of a typical polymer nanocomposite film prepared by the MB-MAPLE method. The film is made of PMMA with the nanoparticles of $NaYF_4$: Yb^{3+}, Er^{3+}. The morphological properties of the prepared polymer nanocomposite films of PMMA: $NaYF_4$: Yb^{3+}, Er^{3+}, PMMA: $NaYF_4$: Yb^{3+}, Ho^{3+}, or PMMA: $NaYF_4$: Yb^{3+}, Tm^{3+} prepared by the MB-MAPLE method were such that the dominant crystalline phase of the embedded nanoparticles of the inorganic phosphor compound (fluoride doped with the RE ions) was the hexagonal β-phase, the most favorable for the efficient visible upconversion fluorescence. The average size of the phosphor nanoparticles was 5-10 nm. They were evenly distributed in the polymer matrix. The average thickness of the films was up to 80 nm.

Being illuminated with a 980-nm laser diode, the films exhibited bright visible up-conversion emission with the spectrum similar to that of the bulk phosphor powder. The quantum yield (QE) of the upconversion emission of the films was estimated using the following approach. QE of the upconversion emission η could be defined as the ratio of the number of the photons of the short-wavelength upconversion radiation generated per unit of time n_{up} to the number of the photons of the infra-red pump radiation n_{pump}

$$\eta = (n_{up}/n_{pump}) \text{ x } 100\% \quad .$$

The order of magnitude of the upconversion QE of the films was estimated with a rather simple but yet reasonably accurate method using the experimental setup in Fig. 8. QE of the film of PMMA: $NaYF_4$: Yb^{3+}, Er^{3+}, for instance, was estimated as

$$\eta = (Pup\ \lambda pump)/(Ppump\ \lambda up) \text{ x } 100\% \sim 0.5\% \ ,$$

where Pup was the measured power of the upconversion emission (at 540 nm); λup was the wavelength of the upconversion emission (~ 540 nm); $Ppump$ was the power of the pump; $\lambda pump$ was the wavelength of the pump radiation (980 nm). The computed value compared well against 3% quantum yield reported for the nanocolloid of similar upconversion phosphor NaYF4: Yb^{3+}, Er^{3+} in Ref. 7.

4. CONCLUSIONS

MB-MAPLE co-deposition of a polymer and inorganic components is a new promising method of making polymer-inorganic nanocomposite films. MB-MAPLE system built at Dillard university, besides one laser beam for MAPLE (for polymer targets), one laser beam for regular PLD (of inorganic targets) can also accommodate the third laser beam for the implementation of the RIR method (and RIR-MAPLE) for the most sensitive organic materials of the biological origin. The system has also the plume direction feedback control to optimize the uniformity of the nanocomposite films. Additional opportunities in terms of the variety of possible coatings can be achieved with the target switching and the substrate manipulation options. The MB-MAPLE system was used to fabricate polymer nanocomposite films with upconversion emission properties. The QE of the films was comparable with similar upconversion phosphors in the form of nanocolloids. That serves as evidence that the MB-MPALE process transferred the nanoparticles of upconversion phosphors in the deposited polymer films without degradation of their optical properties.

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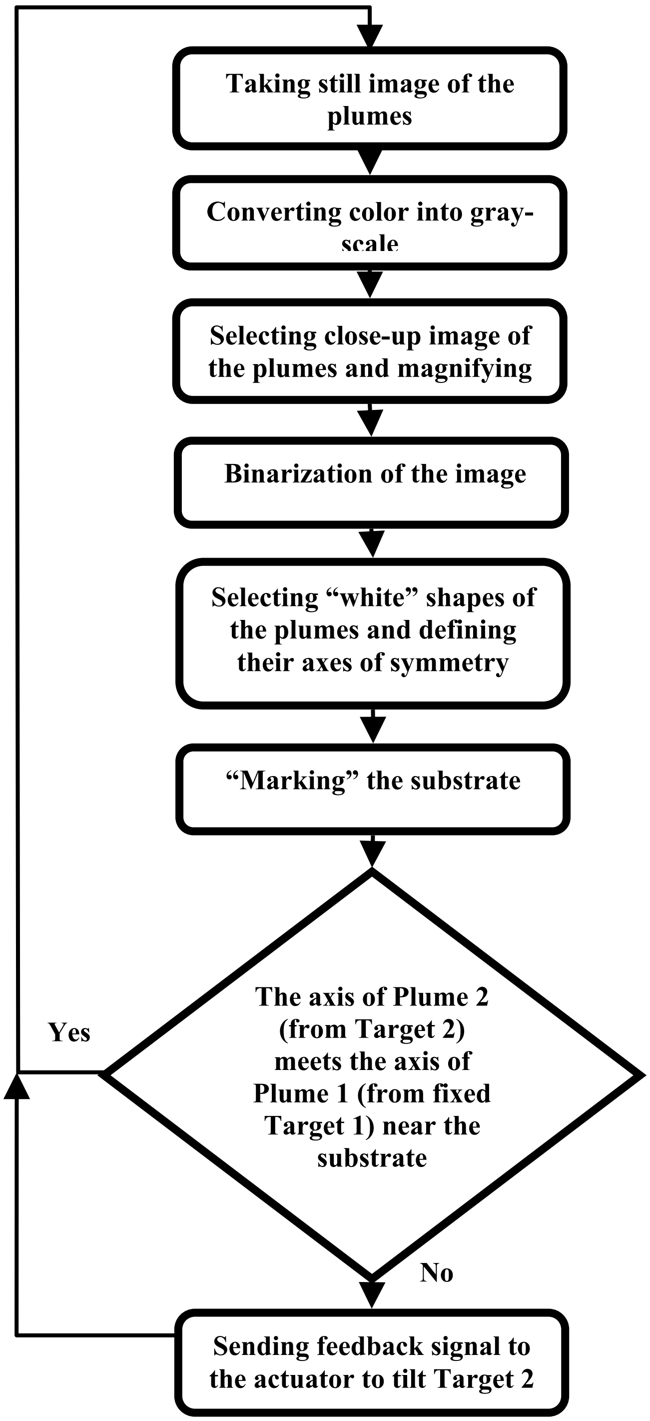

Figure 1. Flow chart of the algorithm of the feedback control of the target tilt angle

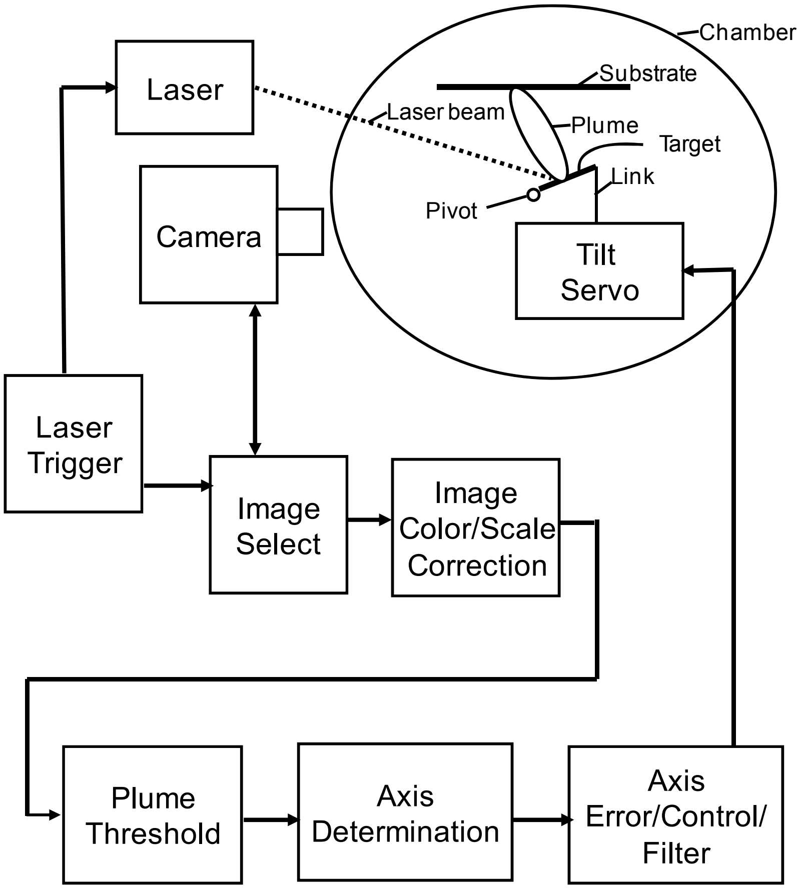

Figure 2. The plume axis control with feedback.

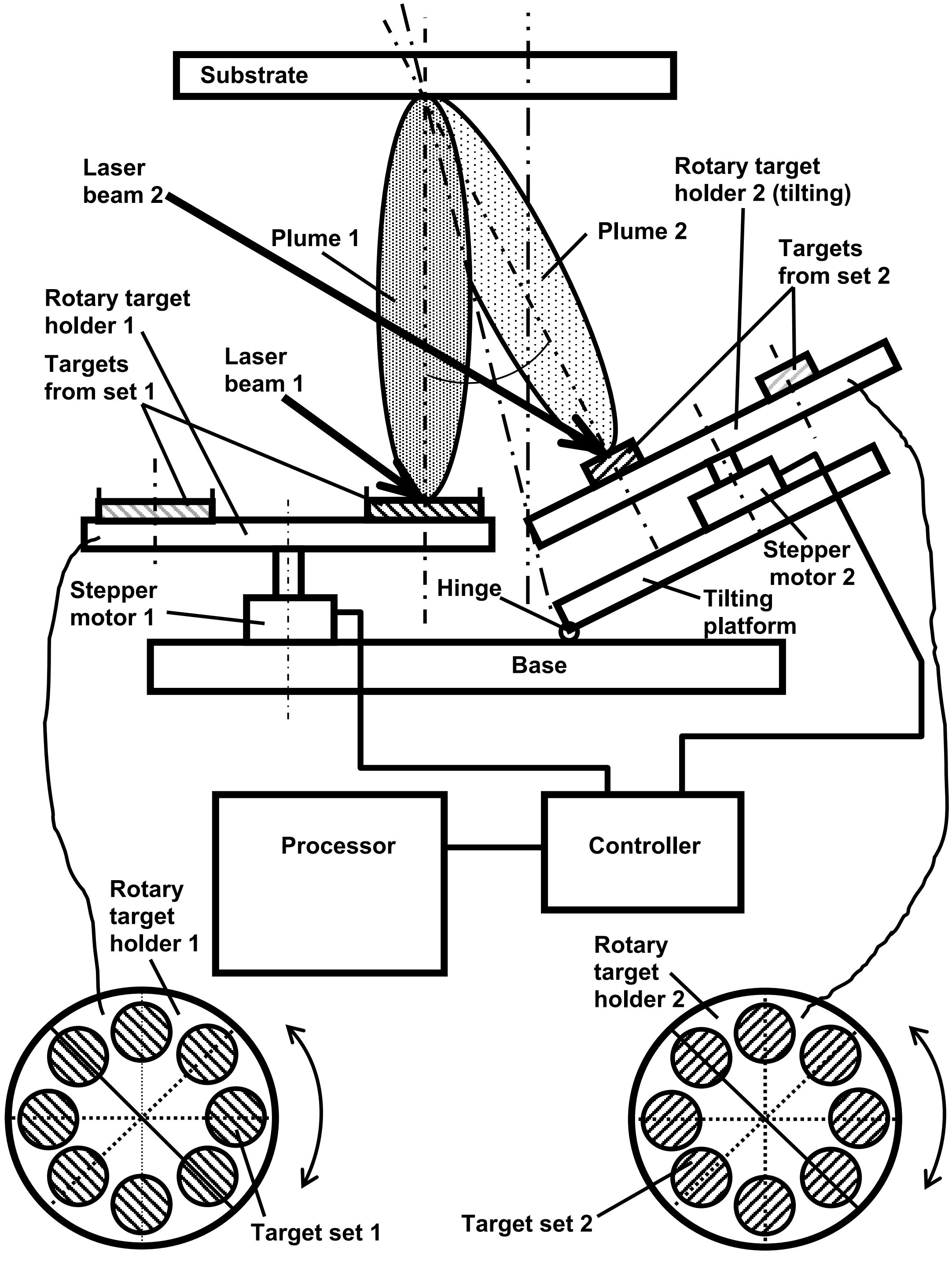

Figure 3. Configuration of the multi-beam deposition system with multiple switchable targets mounted on rotary holders.

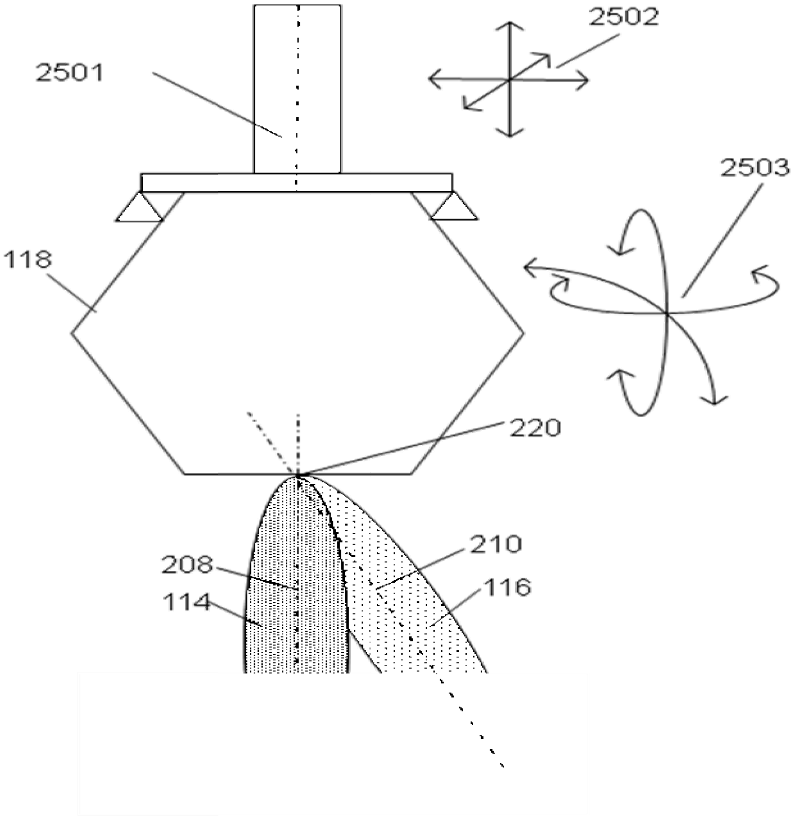

Figure 4. Configuration of the multi-beam pulsed laser deposition with substrate manipulation.

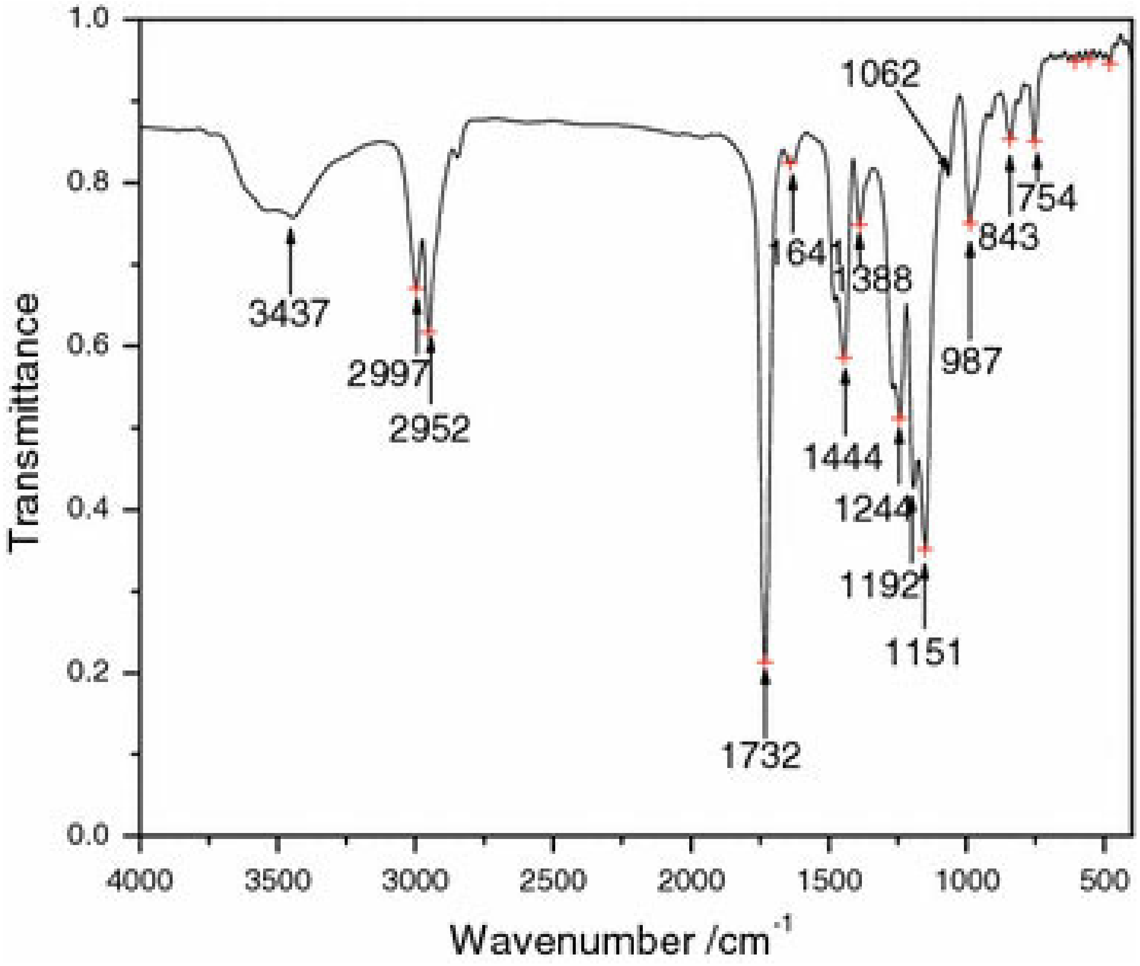

Figure 5. Infrared transmission spectrum of poly(methyl methacrylate) (PMMA) taken with an FT-IR spectrophotometer.

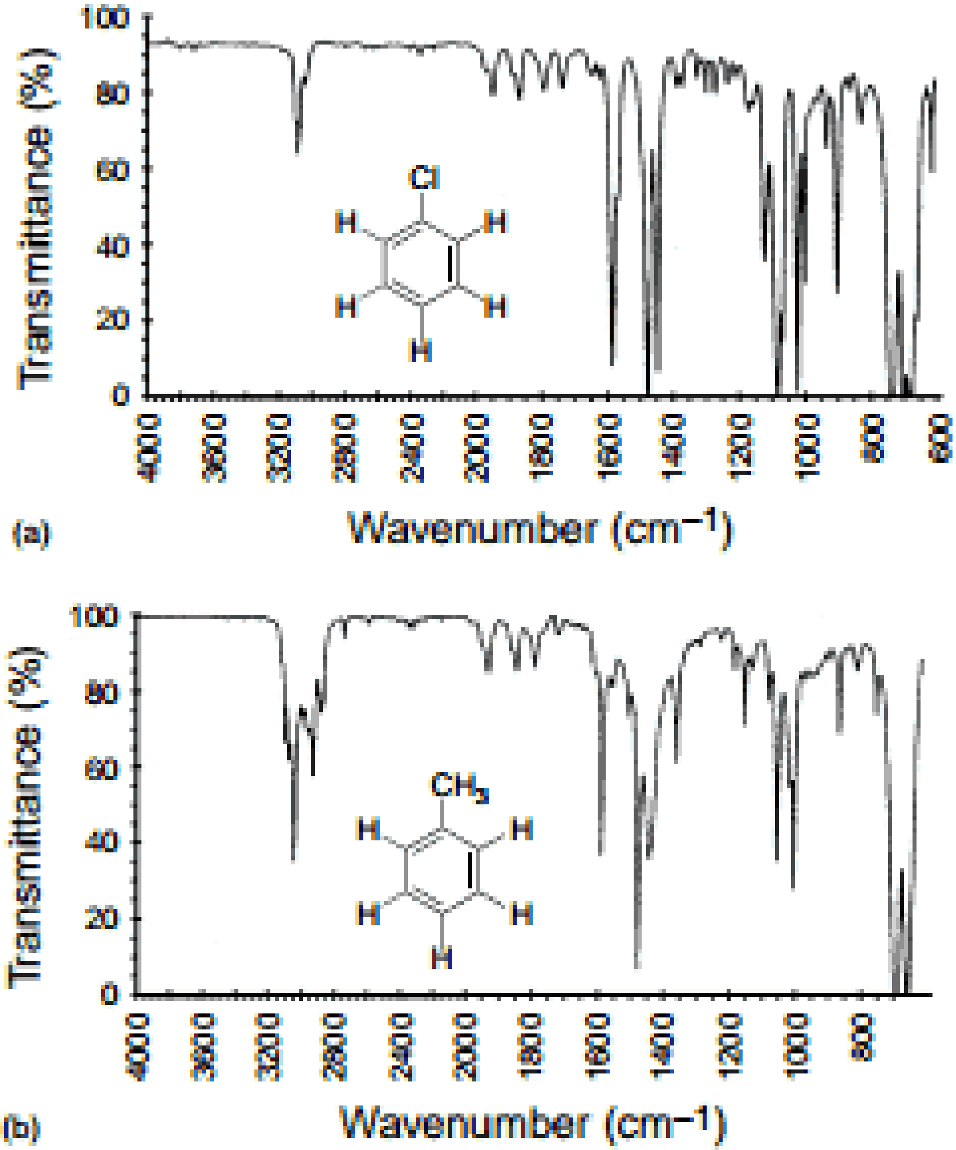

Figure 6. Infra-red absorption spectra of chlorobenzene (a) and toluene (b).

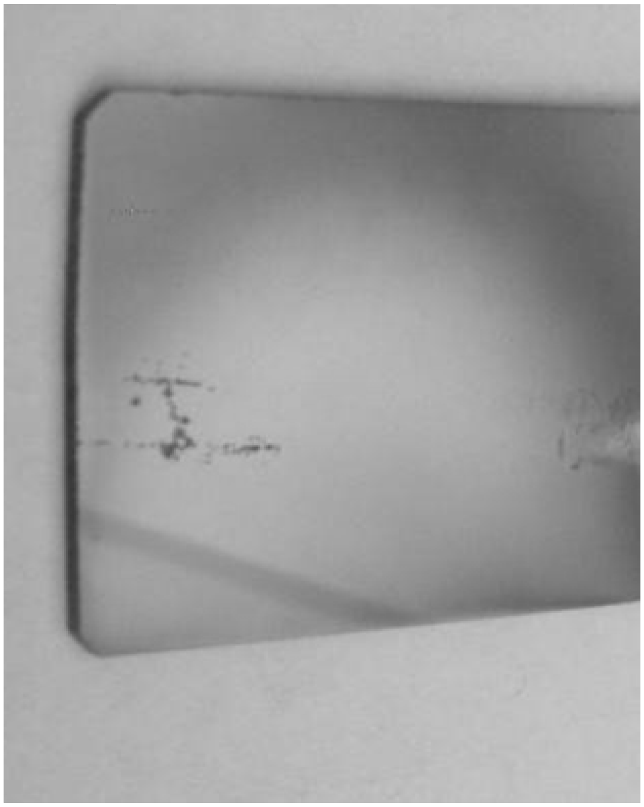

Figure 7. Photograph of the polymer nanocomposite thing film (PMMA + nanoparticles of an upconversion phosphor) deposited on Si substrate using MB-MAPLE.

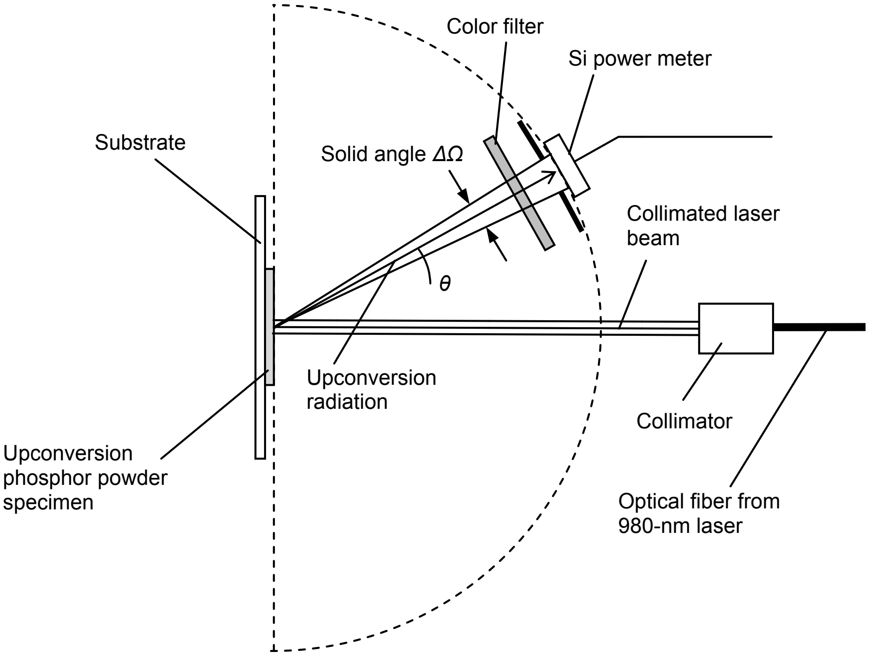

Figure 8. Schematic of the optical setup for measuring the quantum yield of the upconversion emission from the polymer nanocomposite film PMMA: $NaYF_4$: Yb^{3+}, Er^{3+}.