Laser Deposition of Polymer and Biomaterial Films

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1. Introduction to Polymers and Biomaterials

Polymeric materials are characterized by a recurring structural unit, and as such, their molecular weights can cover a broad range, from thousands to millions of daltons. Important organic examples are found in nature, including proteins, nucleic acids, polysaccharides, and rubbers. Polymers are also produced synthetically with a wide range of plastics, elastomers, and fibers made commercially. The physical and chemical properties of polymers are determined by the backbone type, length of backbone, pendant groups that populate the backbone, and any chain cross-linking. Most natural and synthetic polymers can be classified as one of two major types, addition or condensation polymers. Addition polymers are produced by self-addition of a large number of one or more different monomers. Condensation polymers are formed by reactions in which the monomeric units are joined by intermolecular eliminations of small molecules. These broad classifications can have a significant bearing on the type of laser process that can be successfully used to process polymeric materials without significant decomposition. In addition to the primary structure contained in the backbone of the polymer, higher orders of structure can be present that are controlled by intermolecular or intramolecular forces between polymer chains. Some naturally occurring polymers that can exhibit the representative range of structural order types include cellulose, starch, rubber, and proteinaceous materials. Cellulose is a long strap-like molecule formed from repeat units of the simple sugar molecule, glucose. Starch, however, is made of the same glucose units, but joined together in such a way that the molecules form helices. In many proteins, certain sections of molecules can form helical chains, and in a further level of complexity, the helical chain can wrap round on itself to form an almost spherical particle. In rubber materials, the

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Dr. James S. Horwitz is a research chemist in the Plasma Processing section, Surface Modification Branch, Material Science Division at the Naval Research Laboratory in Washington, DC. His current research areas include (1) fundamental mechanisms of laser–solid interactions relevant to pulsed laser deposition of inorganic and organic materials and (2) applications of electronic ceramic films. Materials currently under investigation include high-temperature superconductor (HTS), ferroelectric, CMR materials, transparent oxide electrodes, ferrite thin films, organic thin films for chemical and biological sensors, and organic semiconductors. Applications for these materials include microwave devices based on ferroelectric thin films, passive limiters for microwave front end receivers, microcfulidic valves and pumps based in piezoelectric thin films, oxide electrodes for organic LEDs, and oxide thin films for x-ray particle detectors. This research is expected to (i) demonstrate the feasibility of electronic ceramic materials, protective coatings, and sensor coatings for device applications, (ii) produce a better understanding of the microstructure of these films and how it affects their properties, and (iii) produce a better understanding of the effect that the pulsed laser deposition parameters (e.g., laser target powder, target composition, ambient pressure, and substrate temperature and material) have on resulting film properties. Dr. Horwitz has more than 100 professional publications in reviewed scientific journals.

Bradley Ringeisen received his B.S. (Honors) degree in chemistry (1994) at Wake Forest University. He then was granted a Ph.D. in Physical Chemistry at the University of Wisconsin—Madison in 2000, where he studied surface and bulk interactions that lead to gas solvation and reaction with basic, acidic, and neutral liquids under the direction of Professor Gilbert Nathanson. He then was awarded a National Research Council Postdoctoral Fellowship and worked at the Naval Research Laboratory (NRL) for two years developing laser-based methods to form thin films, patterns, and structures of biological materials. He is currently a staff scientist at NRL researching how laser forward transfer techniques can contribute to fields such as tissue engineering, proteomics, biological agent sensing, and pathology.

long molecules are randomly tangled. This entanglement can also be made permanent by cross-linking polymer chains to stiffen polymer materials or form thermosets. These additional structural complexities further limit the selection of laser-based processing techniques if these complex structures are to be maintained in the films grown.

Biomaterials include any natural or synthetic material that interfaces with living tissue or biological fluids. Even some simple polymers have shown usefulness in some biomedical applications. However, certain physical and chemical characteristics render some materials more desirable than others for biological applications. To complicate things further, the determination of these desirable traits depends on the material's intended use in the body. In all cases, a biomaterial must exhibit biocompatibility with living tissue or biological fluids.

Inorganic biomaterials include materials such as metals, ceramics, and composites whereas organic biomaterials include everything else. While we will try to refer to them as separate categories, there are many materials that satisfy the definition of polymers that can also be considered organic biomaterials and likewise, some of the most important biomaterials, e.g., proteins, also fit the definition of polymers.[1] Table 1 lists some example polymers and organic biomaterials that are important to fabricate in thin film form.

This article describes the use of lasers for growing thin films of polymers and biomaterials such as those listed in Table 1. In section 2 we begin by discussing the issues that are important for polymer and biomaterial thin films. The issues for these materials and their applications in some cases make laser

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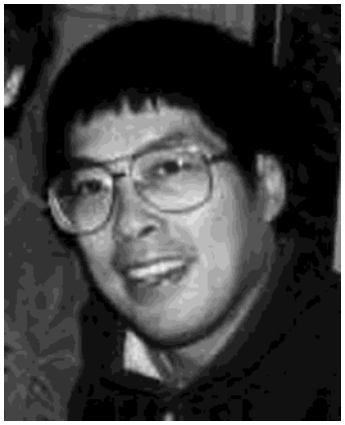

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processing advantageous compared to conventional techniques. But laser processing begins with the interaction of lasers with the target material to be deposited, and the subsequent relaxation of absorbed laser energy and sections 3 and 4 describe that. Section 5 describes ultrashort laser−material interactions, which are mostly used for micromachining because of the extremely small heat-affected zone associated with this interaction. Section 6 summarizes past results on the pulsed laser deposition (PLD) of polymers and biomaterials. Using a UV pulsed laser to deposit a thin film from a bulk target of the polymer or biomaterial is not very effective for nondestructive thin film material growth, and special approaches are required. The laser or the target material is the only input quantities that can be varied, and we discuss both of them. Section 7 describes MAPLE (matrix-assisted pulsed laser evaporation), a laser−material interaction that provides a softer desorption mechanism when compared with PLD because of the use of a composite target of mixed volatility. Resonant IR (RIR) absorption is another laser−material interaction, and this new approach is the subject of section 8. RIR uses an IR laser to selectively couple the laser energy to a vibrational mode in the polymer. Section 9 describes MAPLE direct-write—a laser forward transfer technique with many of the attributes of the basic MAPLE mechanism of section 7. A clear transition is made in this article between past results by PLD and the novel approaches developed in recent years. With the improved capabilities of these new approaches, it is clear that lasers will be indispensable in the processing of polymers and biomaterials, becoming an enabling technology for a range of next generation applications.

Table 1. Examples of Polymers and Biomaterials That Are Important To Fabricate in Thin Film Form

polymers	example thin film applications
polyethylene glycol	biocompatible surfaces
polyurethane	paints
polybutadiene	chromatography stationary phase
poly(methyl methacrylate)	photoresist
polyesters	dental sealants
poly(lactide-*co*-glycolides)	drug delivery systems
poly(tetrafluoroethylene)	chemical resistant surfaces
polyfluoropolyether	hard drive lubricant
polyacrlylonitrile-*co*-vinyl chloride	flame retardant
polyvinylidene fluoride	piezoelectric coating
polysaccharides	pharmaceutical coating
fluoropolyol	chemical sensors
polythiophene	antistatic layer
biomaterials	**example thin film applications**
living and fixed tissue	tissue-based biosensors
living cells	engineered tissue constructs
DNA/proteins	cell signaling arrays and proteomic/genomic microarrays
enzymes	enzyme electrodes
antibodies, oligonucleotides, collagen, elastin	rapid prototyped tissue structures

2. Thin Film Issues for Polymers and Biomaterials

Polymers and biomaterials used as thin films have a wide range of applications in the pharmaceutical, electronics, microsensor, and bioengineering industries. A variety of competing techniques are available to coat polymers and biomaterials and Table 2 provides a comparison of the methods currently available. The first and most basic consideration is whether the application of interest is suitable for parallel or serial processing of polymers. The distinction between serial and parallel processing is important to make clear. In parallel processing, several parts or even all parts of the wafer are processed at the same time, whereas in serial processing, the parts are processed sequentially. There are benefits and drawbacks of each approach for processing polymers that depend strongly on the technique and the application. Table 2 is organized accordingly, and within the two sections of parallel and serial-based processing techniques, five laser-based tools are available. Additional factors that need to be consid-

Table 2. Comparison of Different Techniques Used for Growing Thin Films of Polymers and Biological Materials[a]

coating technique	doctor blade	spin coating	vacuum sublima-tion	dip coat	molecular aggre-gation	PLD[b]	RIR-PLD[b]	MAPLE[b]	aerosol	in situ polymer-ization	ink-jet	MAPLE DW[b]	laser guidance[b]	AFM dip-pen	soft litho-graphy
direct write	N	N	N	N	N	N	N	N	Y/N	Y/N	Y	Y	Y	Y	Y
compatible with broad range of polymeric and biological materials	Y	Y	N	Y	Y	N	Y	Y	Y	N	Y	Y	Y	Y	Y
compatible with composites	Y	Y	N	Y	N	Y	Y	Y	Y	N	Y	Y	Y	Y	Y
room-temperature process	Y	Y	N	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
atmospheric pressure process	Y	Y	N	Y	Y	N	Y/N	Y/N	Y	Y	Y	Y	Y	Y	Y
works with small amounts of material	N	N	N	N	Y	N	N	Y	N	N	Y	Y	Y	Y	Y
monolayer thickness control	N	N	Y	N	Y	Y	Y	Y	N	Y	N	N	Y	Y	Y
film distribution	Y	Y	N	Y	N	N	N	N	Y	N	Y	Y/N	Y/N	Y	N
enhanced film−substrate adhesion	N	N	N	N	Y	Y	Y	Y	N	N	N	Y	Y	N	N
compatible with noncontact masking techniques	N	N	N	N	N	Y	Y	Y	Y	N	Y	Y	Y	Y	Y
multilayer capability without interlayer bleeding	N	N	Y	N	N	Y	Y	Y/N	N	Y	N	N	Y	N	N
does not require dissolution	N	N	Y	N	N	Y	Y	N	N	Y/N	N	Y/N	N	N	N
unaffected by material viscosity and temperature effects	N	N	Y	N	Y	Y	Y	Y	N	Y	N	Y	Y	N	Y
maintenance considerations (H/M,/L)	L	L	M	L	L	H	H	H	M	L	M	H	H	H	ND
technology commercially available (Y/N)	Y	Y	Y	Y	Y	Y	N	N	Y	Y	Y	N	N	N	N
capital costs (H/M/L)	L	L	M	L	M	H	H	H	M	M	M	H	H	H	L

[a] Key: Y = yes; N = no; L = low; M = medium; H = high; ND = not determined. [b] Laser-based techniques.

ered include material viability, biomaterial physicochemical properties, thickness and uniformity, thickness control, patterns and resolution, adhesion, and solubility. Next-generation applications place increasingly stringent demands on film controls making laser-based techniques more attractive when compared to other conventional techniques.

Pulsed laser-based techniques lend themselves to both parallel (pulsed laser deposition, PLD; resonant infrared pulsed laser deposition, RIR-PLD; matrix assisted pulsed laser evaporation, MAPLE) and serial processing (MAPLE direct-write, laser guidance) of polymers, and they largely compete with techniques that require dissolution of polymers in solvents and intimate wetting of polymer solutions applied to the substrate to be coated. This is undesirable for many applications, as it is difficult to control the film thickness and morphology and it makes it difficult to deposit multilayer films. For solvent-based techniques, the solvent controls the mobility of the polymer on the substrate surface. This makes the morphology of the film dependent upon a number of factors, including solvent evaporation rate, surface wetting and spreading of the solvent, and surface roughness. The wetting effects are difficult to control and require careful surface cleaning procedures to ensure reproducibility. As a consequence of the solvent, thin films are found to contain nonuniformities. For example, the appearance of individual ink-jet spots as round dots with edges that are different in thickness than in the middle is due to solvent evaporation rates being different at the edge of the drop than in the middle and possibly from splash down effects which do not have sufficient time to recover before the solvent evaporates.

From the laser-based techniques listed in Table 2 that offer parallel processing, MAPLE, PLD, and RIR-PLD all require a shadow or contact mask technique for discrete coating capability to protect areas where coating is undesirable. For highly dense arrays of devices that are coated as integrated array structures (i.e., not individual elements that are later assembled into an array), these techniques become increasingly undesirable as the array number size increases. Laser-based direct-write techniques, such as MAPLE DW and laser guidance approaches, have demonstrated the ability to form patterns and three-dimensional structures of different biomaterials (living cells, active proteins and antibodies), and each may find a niche or more general application that will displace currently used deposition tools.

Not all polymer materials can be dissolved and processed in common organic solvents. For these materials, solution-based deposition techniques are not applicable, and alternative techniques are needed. In some cases, polymers can be formed in situ by chemical reactions from monomer material (either thermally or electrochemically). For example, conducting polymers such as polyaniline can be electrochemically grown in situ to a conducting electrode, which after film growth results in a chemiresistor sensor. In another application, the distal ends of individual optical fibers within a bundle of fibers have been coated by photopolymerization.[75] The preceding examples are quite specific techniques that are remarkable within their domain, but widespread application is limited. PLD of solid polymers has limited applicability to polymers but has been demonstrated with reasonable success for Teflon and other addition polymers. For increasingly structure-sensitive materials such as biological materials, PLD will probably never develop to allow biological materials to be processed without damage. Recently, resonant infrared-PLD (RIR-PLD) of a variety of polymers has been successfully demonstrated. In this technique, the laser wavelength is selected that corresponds to a specific vibrational absorption band in the infrared spectrum of the polymer. This technique has been applied with very promising results to processing polymer materials that previously resulted in significant polymer decomposition under other laser wavelength processing conditions.

3. Interaction of Laser Radiation with Polymers and Biomaterials

Shortly after the discovery of the laser, researchers began irradiating almost every conceivable target material and phase for novel basic physical and chemical study in addition to new applications. Even thin-film deposition by a pulsed ruby laser was explored early on and some of its eventual benefits were realized.[2] Laser deposition of polymers and biomaterials present an especially interesting case study because the pulsed laser deposition of materials usually uses the high power (e.g., pyrolytic chemical vapor deposition) or short penetration depth (ablative) character of the laser−material interaction, and these are usually incommensurate with their nondestructive processing. Even at low fluences, some polymers and biomaterials are extremely photosensitive. With an improved understanding of the laser−material interaction and the discovery of new laser−material combinations, lasers have proven to be powerful tools in the novel processing of polymer and biomaterial films.

What makes the laser−material interaction so unique is the multitude of possible laser and material parameters that can be varied and the range over which they can be varied. For example, the laser wavelength can be changed from selective absorption resonant with specific energy transitions to pyrolytic decomposition. The fluence and power can be similarly varied, though for the materials that are the subject of this article, low fluence and low power is preferred. The laser pulse width can be infinite (continuous wave) to femtosecond. The range of possible materials that can be varied are similarly large, but in most past work, they have only included bulk targets of the material to be deposited. In later sections, it will be shown that it is possible to synchronously optimize both the laser and the material to achieve a novel route to desorption and thin film deposition.

4. Laser Energy Deposition and Relaxation

While the development of a quantitative theory of desorption of material from a laser irradiated target is in its infancy, our qualitative understanding begins

with and is based on the deposition of photon energy. In the pulsed laser evaporation of materials, the response of the target is highly dependent on the characteristics of the laser source. The instantaneous intensity of laser absorption at any given depth is best described by the Beer−Lambert law

$$I(x,y,z) = I_o(x,y)e^{-\alpha.z}$$

where I_o is the incident intensity at the surface of the target, α is the absorption coefficient, and z is the depth. In this simple expression, α depends on the target material, wavelength of the radiation, and the intensity. When combined with the heat conduction equation

$$\rho \cdot c \cdot (\partial T(\mathbf{r},t)/\partial t) = k \cdot \Delta T(\mathbf{r},t) + S(\mathbf{r})$$

where ρ is the density, c is the specific heat, k is the conductivity, $S(\mathbf{r})$ is the source term, the Beer Lambert law can be very useful for describing thermal processes at surfaces. There are two key parameters that are integral for the desorption and deposition of intact material from the target, and their dependence is not obvious from neither the Beer−Lambert law nor the heat conduction equation. These key parameters are the laser pulse width and wavelength. Especially for polymers and biomaterials, the laser pulse width and wavelength can be adjusted to have a resonant effect and these topics are treated in sections 5 and 8, respectively.

The absorption of the incident radiation by the target electrons produces localized excitations that will decay via radiative and nonradiative processes. If sufficient photonic energy is present, electronic excitation can lead directly to photochemical decomposition. If the density of thermalized energy is above a threshold value, thermal chemistry can be observed. But there can exist a regime where the thermal motion of the target species can overcome the cohesive energy of the target and surface binding energy and be desorbed, resulting in a vapor phase which can be collected to produce an adherent film. Because of the potential applications of polymer and biomaterial thin films and the difficulties with conventional techniques, researchers have explored the parameter space of laser−material interactions to find this regime. An overview of past work in this area is given in section 6. In addition, as will be described in sections 7, 8, and 9, our group exploited novel conditions for the laser−material interaction to produce high quality thin films. The MAPLE mechanism is used: (1) in a vacuum similar to PLD to nondestructively desorb polymers and biomaterials (section 7) from matrix targets and (2) in ambient air in a laser forward transfer configuration similar to laser induced forward transfer, or LIFT, to forward transfer polymers and biomaterials (section 9). Last, the resonant infrared interaction with vibration modes of the target material can, in the exact same situation as the photochemically destructive pulsed laser deposition technique, produce nondestructive desorption of extremely large molecular weight polymer thin films. Table 3 lists some of the major infrared absorption wavelengths of organic groups and bonds. Section 8 will show that with selected polymers, resonant infrared interaction with the C−H and the O−H produces high quality polymer thin films

Table 3. Table of Infrared Absorption Wavelength of Various Groups and Bonds

group	wavelength region (μm)	group	wavelength region (μm)
O−H	2.94	C═O	5.80
N−H	3.00	C═N	5.94
C−H	3.36	C═C	6.07
C−O	9.67	C═S	6.57
C−C	11.49		

5. Ultrashort Laser Interactions

Ultrashort laser pulses (ps−fs) offer several advantages in the pulsed laser deposition of materials.[3] The short interaction time causes the energy to be deposited into a thin layer of the material. The confinement can lead to the creation of high energy density plasma. Ejection of the material from the plasma occurs on a time scale that is shorter than the thermal conduction time scale, and as a result, there is less collateral damage compared to longer (ns) pulsed interactions. Because of the short pulse duration, shielding of the laser by the plasma is absent, and the ablation efficiency is high compared to nanosecond laser pulses. Optimization of the laser parameters for material removal involves balancing of the pulse duration, intensity and repetition rate.

There are three distinct features of the ultrashort laser−insulator interaction.[4] First, there is insufficient time for typical impurity driven optical breakdown normally observed in ns laser pulses. Instead, the high intensities reached in ultrashort pulses leads to plasma formation by nonlinear, multiphoton absorption and ionization. Since the laser energy is deposited into electrons much faster than it can be transferred into the bulk material, more of the energy is transferred into kinetic energy of the ablated species rather than the thermal energy of the bulk, thus minimizing collateral damage of the bulk material. This latter region is typically referred to as the heat affected zone. The plasma formation, and expansion that takes place in ns laser pulse interaction, leads to absorption and heating of the plasma by the laser. For shorter pulses, the minimal expansion results in the formation of plasma that serves to reflect rather than absorb the incident radiation. There is considerable controversy over the evaporation mechanism in the ablation of polymers, i.e, the importance of thermal versus photochemical pathways. The reduced collateral damage observed in ultrashort-pulse lasers ablation requires the presence of both thermal and nonthermal mechanisms.[5]

In general, in pulsed laser ablation, the transition from the solid phase to the gas phase can occur in a stepwise fashion. Laser heating of the solid results in the formation of a liquid state. Boiling occurs when the vapor pressure of the liquid exceeds the ambient pressure. If the temperature of the liquid reaches a critical temperature, the material can undergo what is sometimes called a phase explosion.[6] Sublimation

can also occur if the bulk material reaches a temperature that is higher than the critical temperature. However, it is observed in many cases that the laser heating produces nonthermal characteristics in the evaporated material. The kinetic energies of the ejected species are often characterized by temperatures that are in excess of reasonable thermal surface temperatures.

In all materials, the energy relaxation process is characterized by a relaxation time to reach thermal distribution. There are several other time scales that are important to consider in the removal of material. These time scales are closely related to the threshold for material removal, with higher thresholds observed in materials with higher thermal conductivity. The material removal times are determined by mass transport. Ablation times are long compared to laser pulses since the time scales are determined by hydrodynamic and acoustic processes. When the transport time is long compared to the relaxation time, a characteristic temperature can be calculated, and the evaporation can be described in terms of equilibrium thermal properties. However, in the short pulse case, thermal equilibrium is not reached, and the description of the process has to involve thermodynamically metastable states, superheated liquids and supersaturated vapors.

For materials, investigation of UV laser interactions with polymers revealed that the desorbed products were not the same chemical composition and structure as the irradiated material.[7,8] When the products of the UV ablation of polymers have been analyzed, it is observed that the laser produces atoms, diatomic and polyatomic molecules, and small fragments of the polymer. The products are formed by either a photochemical or photothermal mechanism. To date, there are only a few investigations on the effect of the ultrashort laser pulse width on the ablation of polymers.[9−11] The main advantage to using ultrafast laser pulses in polymers is that heat diffusion is minimal and energy lost to the material is minimized. Therefore, machining can be done to a high precision with minimal collateral damage. Also, it is observed that the ablation threshold is reduced, which can be as much as 2 orders of magnitude lower when comparing nanosecond to femtosecond pulses.[12]

The general photochemical mechanism for polymer ablation involves a vertical transition to a metastable, weakly bound or dissociating state. On the time scale of a molecular vibration, photochemical dissociation can compete with both radiative and nonradiative deactivation processes. However, if the initial absorption that results in electronic excitation is followed by rapid relaxation to a vibrationally excited ground state, this can produce local heating, melting and vaporization,[13] or a photothermal process. One can construct reasonable pathways to the observed products using either mechanism, which has made a unique assignment difficult.

In the excimer laser etching of polyimide, Brannon et al. looked at the wavelength dependence (248−351 nm) of etching as a function of laser fluence. The threshold was observed to be independent of wavelength; therefore, the authors conclude that the simplest physical model consistent with the etching data attributes ablation to an intense local heating.[14]

6. Pulsed Laser Deposition of Polymers and Biomaterials

6.1. Origins of Pulsed Laser Deposition

One of the principal challenges in solid-state physics, surface chemistry, and materials science is the discovery and application of novel materials and their incorporation in devices for use in areas as diverse as biophysics, optoelectronics, and nanotechnology. As the requirements for size and materials properties become more stringent, novel techniques for thin film deposition become very important. Since their introduction in 1962, pulsed lasers were recognized as a flexible and powerful tool for material processing applications. One of the most technologically important applications of the interaction of laser light with a solid material is PLD. The fact that a pulsed laser beam is able to readily vaporize almost any material suggested that it could be used to deposit thin films. The first demonstration of PLD dates to 1965, when Smith and Turner demonstrated the growth of thin films of various inorganic and organic materials using a ruby laser.[2] Since then, PLD has become increasingly popular within research laboratories as a method of producing thin films of novel materials, although it has yet to be used in manufacturing environments.

Figure 1 shows a simple schematic with the basic elements comprising a PLD system. An intense laser pulse passes through an optical window in a vacuum chamber, and it is focused onto a solid or liquid surface, subsequently referred to as the target. There the laser pulse is absorbed, and above a given power density, significant material removal will occur in the form of an ejected forward-directed plume. The threshold power density needed to generate such plume depends on the target material, its morphology, the laser pulse wavelength, and the laser pulse duration. For a more detailed discussion of the PLD process, see Chrisey and Hubler.[15]

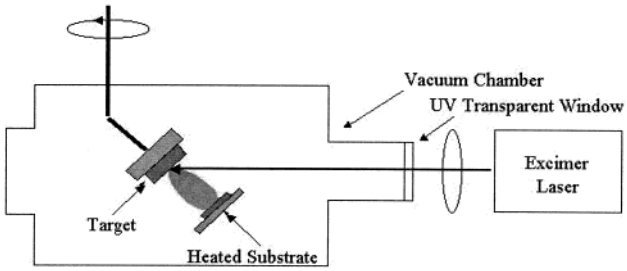

Figure 1. Schematic diagram showing the basic elements of a PLD deposition system.

PLD for thin film growth offers many advantages: (i) the energy source (laser) resides outside the vacuum chamber, which, in contrast to vacuum-installed devices, provides a much greater degree of flexibility in materials use, geometrical arrangements, and adjustment of growth parameters; (ii) almost any material in solid or liquid form can be ablated; (iii) the pulsed nature of PLD means that

film growth rates and film thickness can be controlled to a high degree; (iv) the amount of evaporated target material is localized only to that area illuminated by the laser focused spot; (v) under optimal conditions, the ratios of the elemental components of the target and film are the same, even for chemically complex systems; (vi) the kinetic energies of the ablated species lie mainly in a range that promotes surface mobility of the species upon arrival to the substrate; (vii) the ability to produce species with electronic states far from chemical equilibrium opens up the possibility to produce novel or metastable materials that would be impossible under thermal conditions.

6.2. Early Applications of PLD for the Growth of Organic and Polymer Thin Films

Attempts to deposit thin films of organic and polymeric materials by PLD date back to the first report by Smith and Turner,[2] who showed the growth of thin films of fuchsine (an organic dye) and Ni−dimethyl glyoxime (a pigment used in paints and cosmetics). Despite this early report, not much work was done in PLD of organics and polymers for the next 20 years until Hansen and Robitaille demonstrated the use of pulsed UV lasers for depositing films of several polymers.[16,17] They studied a variety of polymer systems, such as polyethylene, polycarbonate, polyimide and poly(methyl methacrylate) or PMMA. Their results showed an improvement on the ablation behavior and film morphology as a function of decreasing wavelengths. Hansen and Robitaille further observed that the film quality is enhanced by working at laser energies near the ablation threshold of the polymers. However, they also noted a decrease in the molecular weight of all the films that they prepared.

One polymer system that attracted much attention early on was polytetrafluoethylene or PTFE, Teflon. Extensive work on deposition of PTFE thin films by laser ablation was performed by Blanchet et al. [18−20] They surmised that film formation occurs by way of a laser-induced pyrolytic decomposition, followed by repolymerization. Such unzipping and subsequent reconstruction of the polymer chains is observed for addition polymers deposited by thermal evaporation processes. However, during UV laser ablation, the fragmentation of the polymer chains can also occur due to the high photon energies, which tend to exceed the binding energies of most common types of bonds present in the chains. A distinction between photolytic and pyrolytic processes in the bond scission is to be made. In general, it depends on the identity of the polymers and processing parameters such as laser wavelength, laser fluence, and laser pulse duration. Work done by Srinivasan et al.[21] describes the importance of the photolytic scission of bonds during polymer ablation of PMMA surfaces irradiated with 193 and 248 nm laser pulses. However, a review article by the same author and other reports suggest that for most polymers, with the exception of PMMA, thermal dissociation mechanisms play an important role.[22−24] Znotins et al.[25] pointed out that either a photolytic or a thermal process dominates the ablation mechanism depending on the absorption cross section for the ablated material at the applied wavelength. Blanchet et al.[20] proposed a thermal ablation mechanism of PTFE when ablated with a pulsed UV laser, based on the similar mass distribution observed for the ablated species when compared to those obtained during pyrolytic decomposition of PTFE. They pointed out that UV pulses absorbed by the polymer provide an efficient thermal source. On the basis of this, the observed decrease on average molecular weight can be attributed to the partial repolymerization of the thermally unzipped monomers.

6.3. Overview of Thin Films of Organic and Polymeric Materials Grown by PLD

In the following subsections, we will discuss some of the current results and trends in PLD of polymer and organic materials. The discussion will follow a chronological order within each subclass of materials.

6.3.1. PLD of Addition Polymers

The deposition of thin films of addition polymers is of great technological relevance, given their numerous uses and applications. References in the literature for thin films of addition polymers grown by PLD can be found for PTFE, PMMA, and polyvinylidene fluoride (PVDF).

6.3.1.1. Poly(tetrafluoroethylene) (PTFE) Thin Films. PTFE is an inert polymer with low dielectric constant and high mechanical strength, which could play a very important role in the electronics industry, and also as a tribological coating for mechanical components. However, due to its lack of solubility, its application in these areas has been limited. Various techniques have been employed to deposit thin films of PTFE, such as vacuum evaporation, sputtering, and plasma polymerization of fluorocarbon monomer gases. None of these techniques have resulted on satisfactory PTFE films. On the other hand, its been shown by Blanchet and co-workers that high quality, chemically intact PTFE thin films can be deposited by PLD.[19,20] Similar results were obtained by Norton et al.,[26,27] who demonstrated the growth of crystalline PTFE films as a function of substrate temperature. Furthermore, by evaluating their films using transmission electron microscopy, they were able to show that the axis of the PTFE molecular chains on the crystalline films was aligned parallel to the film−substrate interface plane. Ueno and co-workers demonstrated the deposition of crystalline PTFE films using an F_2 excimer laser in 200 mTorr Ar background.[28] They were able to demonstrate smooth PTFE films by heating the substrate to 97 °C during deposition. Using a XeCl excimer laser (308 nm) and a CW CO_2 laser (10.6 μm), Inayoshi et al. demonstrated the ability to deposit PTFE films by PLD and evaporation of PTFE bulk targets respectively.[29] The PTFE films evaporated by the CO_2 laser showed identical composition and structure to that of the PTFE target, while those deposited by the ablation of the PTFE targets using the 308 excimer emission were fluorine deficient. Similarly, Li et al. reported growing thin crystalline PTFE films by PLD at 248 nm, under an Ar back-

ground pressure of 75−750 mTorr (0.1−1.0 mbar) and at a substrate temperature of 300 °C.[30] In this work, the authors also discussed the high deposition rates achievable with PLD (up to 16 nm/sec) which are much higher than those obtained by other techniques for depositing PTFE films.

PTFE films have been grown by PLD using synchrotron radiation etching as demonstrated by Katoh and Zhang.[31] Their work showed that crystalline PTFE films with smooth surface morphologies and identical chemical composition to that of the target can be deposited with the substrate at room temperature. Further work by the same group showed that the crystalline PTFE films deposited by synchrotron radiation had the polymer chains aligned perpendicular to the surface substrate, whereas the molecular axis of the PTFE films deposited by UV-PLD are parallel to the substrate surface.[32,33] The authors explain this difference on the basis of the nature of the species ejected from the PTFE target during laser ablation versus synchrotron radiation etching. The unzipping of the PTFE molecule during laser ablation yields mainly radical fragments of the monomer unit, which undergo polymerization on the substrate surface. As a result, the polymer chains grow parallel to the surface. In the case of the PTFE films deposited by synchrotron radiation etching, Zhang et al.[32,33] have shown that the interaction of the synchrotron radiation beam with the PTFE target results in the ejection of molecular oligomers of perfluoro-*n*-alkanes. The perfluoro-*n*-alkane oligomers upon their crystallization form lamellar structures with molecular axes normal to the substrate surface.

The highly oriented PTFE films generated by PLD can be used for some interesting applications. Luo et al.[76] have demonstrated the use of highly oriented crystalline PTFE films to align liquid crystals for display applications. This work showed that the orientation of the PTFE crystals along the substrate plane depends on the geometry of the substrate with the target. When the surface of the substrate was oblique to the target surface, the PTFE chains are parallel to each other, while when the surface of the substrate is parallel to the surface of the target, the PTFE chains are radially oriented in the substrate plane. Another example of the unique properties of the PTFE films made by PLD was provided by Schwödiauer et al.,[34,35] who compared the charge stability of PLD grown PTFE films against that of commercially available Teflon-PTFE foils. They showed that the structure of the PLD PTFE films strongly depends on the target material, ranging from highly crystalline films showing only structural phase transitions to films strongly deviating from PTFE foils, with structural characteristics comparable to plasma-polymerized fluorocarbons. Moreover, the authors measured the dielectric loss of the highly crystalline PLD films and found that it compares favorably with conventional PTFE foils. These results indicate that the PTFE films by PLD might be useful for new applications in miniature electronic devices.

6.3.1.2. Silicon-Based Polymer Films. Silicon-based polymers are difficult to process into thin film form due to the fact they are highly insoluble in most organic solvents. The first silicon-based polymer thin films deposited by PLD were reported by Suzuki et al.[36] Thin films of polymethylphenylsilane (PMPS) were made using a XeF excimer laser (351 nm) under N_2 partial pressures of 250 mTorr. The resulting films all showed smaller molecular weights than the original polymer. The same group has also reported on the deposition of hexaphenyldisilane (HPDS) thin films by PLD.[37−39] It should be noted that all the silicon-based polymer films deposited by this group differ from the starting materials and show various levels of chemical decomposition caused by the PLD process.

6.3.1.3. Other Addition Polymer Films. Blanchet et al.[40,41] have shown the growth of PMMA films using the fourth harmonic emission of a Nd:YAG laser (266 nm). Similar to PTFE, they observed that the substrate temperature during deposition played an important role in determining the morphology and molecular weight of the resulting films.

Jiang et al.[26] have demonstrated the growth of polyvinylidene fluoride (PVDF) films by PLD using a KrF excimer laser (248 nm). The films were deposited under various substrate temperatures ranging from 25 to 200 °C. The morphology of the film surfaces improved with deposition temperature; however, all the PVDF films deposited in this work were amorphous.

Kale and co-workers prepared films of polyphenylene sulfide (PPS) polymers by PLD using a KrF excimer laser (248 nm).[42] PPS is a technologically relevant material given its exceptional chemical and mechanical properties and high-temperature operating range (−170 to 190 °C). The depositions were either conducted at room temperature or at 90 °C. The later was chosen since it was just above the glass transition temperature of PPS. By measuring the index of refraction of the PPS films, the authors determined an increase of the density of the PPS films as a function of deposition temperature. A more recent work by Das et al.[43] demonstrated an enhancement of the crystallinity of the PPS films by growing the films at substrate temperatures of 125 °C.

Other examples of addition polymer films deposited by PLD include polyimide, and polystyrene (PS). Chaudhari and Rao[44,45] reported on the growth of polyimide thin films by PLD on GaAs substrates heated to 200 °C during deposition. The resulting films were smooth and showed Schottky barrier-like behavior after Ag electrodes had been evaporated on their surface. Deposition of PS films by PLD using a PS target doped with anthracene (3.8 wt %) and a XeF excimer laser (351 nm) has been reported by Tsuboi and Itaya.[46]

6.3.2. PLD of Optoelectronic Organic and Polymer Materials

In the following subsections, we will discuss some of the most relevant results in the use of PLD for growing thin films of polymers with optoelectronic properties such as conducting polymers, semiconductive polymers, and luminescent organic materials.

6.3.2.1. Polyperinaphthalene or PPN. PPN belongs to the class of highly conducting organic

polymers with important applications in the electronics industry. PPN differs from typical conductive polymers in that it is intrinsically highly conductive without the need for doping to form charge-transfer complexes. PPN films have been grown by PLD by ablating 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) targets using the fourth harmonic emission (266 nm) from a Nd:YAG laser.[47] In this work, Yudasaka and co-workers showed that for fluences above 10 mJ/cm^2, the resulting films did not contain PTCDA. The PPN films exhibited smooth surfaces; however, X-ray diffraction analysis indicated that the crystallinity of the films was rather low. Nishio et al.[48,49] have also deposited PPN films by ablating a PTCDA target with a XeCl (308 nm) excimer laser. By heating the substrates above 200 °C, the authors showed that the resulting films exhibited a significant increase in conductivity. The highest conductivities (10^{-1} S/cm) were obtained for those films deposited at 300 °C. FTIR and Raman analysis of the films indicate that they all contain PTCDA molecules and radicals such as perylene fragments on various amounts, depending on the deposition temperature. Depositing at higher temperatures helps mitigate this problem.

6.3.2.2. Polyacrylonitrile (PAN) Thin Films. Polyacrylonitrile (PAN) thin films have been deposited under vacuum and at room temperature by PLD using various excimer laser wavelengths at 193, 248, and 308 nm, as reported by Nishio et al.[50,51] The authors evaluated the effect of laser wavelength and laser fluence on the structure and properties of the films. PAN was selected for this study since its changes in dielectric and electric conductivity properties are well characterized once it undergoes pyrolytic processing owing to the existence of nitrile groups in its structure. Only those films deposited using a XeCl excimer laser (308) nm retained the original PAN structure. Furthermore, the films deposited at 308 nm were highly crystalline, while the films deposited at 193 nm (ArF) and 248 nm (KrF) were amorphous.

6.3.2.3. Electrically Conducting Polymers: Polyacenic Semiconductive (PAS) and Polythiophene Thin Films. Polymers such as polyacenic semiconductive (PAS) exhibit a wide range of electrical conductivities (10^{-10}−1 S/cm) and are stable in air depending on the pyrolytic processing temperature. Nishio et al.[52] studied the growth of PAS thin films by PLD as a function of substrate temperature with the goal of controlling the film's chemical structure and electrical properties. Their results showed that PLD of bulk phenol-formaldehyde (PF) targets using a 308 nm XeCl excimer laser resulted on PAS films with electrical conductivities significantly higher than that of bulk PAS material processed at the film growth temperatures.

Another example of a conductive polymer material is polythiophene. Nishio et al.[53] have shown the growth of polythiophene thin films under vacuum and at room temperature by ablating a 2,5-dichlorothiophene target with a 248 nm KrF excimer laser. The resulting films exhibited electrical conductivities ranging from 10^{-7} S/cm up to 10^{-3} S/cm after doping with iodine. The doping was performed by exposing the films once deposited to I_2 vapors in a glass cell.

6.3.2.4. Luminescent Organic Materials. Electroluminescent organic materials have attracted a great deal of attention as their use in thin-film form for the fabrication of organic light emitting diodes (OLED's) has become well established. The use of PLD to deposit these types of materials is complicated by the fact that their structures cannot be subjected to the same unzipping and repolymerization process that works with addition polymers. In general, the perfect reconstruction upon deposition of the organic molecular structures for these materials is never observed once ablated at laser fluences higher than their ablation threshold. Matsumoto et al.[54] have shown that PLD of organic electroluminescent materials is possible at laser fluences near the ablation thresholds of these materials. Using a 248 nm KrF excimer beam, Matsumoto and his team demonstrated the growth of amorphous copper phthalocyanine (CuPc), Aluminum tris-8-hydroxyquinline (Alq_3) and 4-dialkylamino-4′-nitrostilbensen (DANS) thin films by PLD. The authors verified the electroluminescent properties of the CuPc and Alq_3 films by fabricating double layer electroluminescence cells consisting of CuPc and Alq_3 layers as a hole-transport and a luminescent layer, respectively, on top of SnO_2 electrodes evaporated on a glass substrate. Al electrodes were then evaporated on the top Alq_3 layer. The resulting double-layer electroluminescent devices produced efficient emission at 500 nm. In a subsequent report, Ina et al.[55] described the growth of crystalline CuPc and DANS thin films by PLD under the same conditions, but in addition by applying three different methods during film deposition, i.e., substrate heating, irradiating the film with a second laser, and applying a DC electric field between the target and the substrate. Stevens et al.[56] have also shown the growth of luminescent thin films of the conjugated polymer poly(*p*-phenylenevinylene) (PPV) by PLD of a PPV target using the third harmonic emission of a Nd:YAG laser (355 nm). The authors measured photoluminescence spectra for the PLD films that were very similar to that of spin coated PPV.

6.3.2.5. Pentacene. The use of organic materials as active layers for making thin-film transistors has received considerable attention lately. One organic material that has been used for these applications is pentacene. Salih et al.[57−59] has reported on the growth of pentacene thin films under vacuum and at substrate temperatures ranging from 30 to 100 °C by PLD of pentacene targets using a KrF excimer laser (248 nm). The resulting films showed surface roughness that decreased as a function of deposition temperature. In fact, the electrical conductivity of the films was higher than that of pentacene films thermally evaporated onto substrates at similar temperatures. Furthermore, the pentacene films grown by PLD exhibited very large field effect mobilities and very small threshold voltages, 4×10^{-2} cm^2 V^{-1} s^{-1} and 0.3 V, respectively. These results are of considerable significance for practical applications.

6.3.2.6. Other Examples of Optoelectronic Organic Materials Deposited by PLD. Tsuboi et al.[60] deposited poly(N-vinylcarbozole) (PVCz) thin films by PLD of PVCz targets under vacuum at room temperature using three excimer laser wavelengths (248, 308, and 351 nm) as a function of fluence. The resulting films were amorphous and their surfaces showed numerous particle-like features. The optimum ablation conditions were found using a 351 nm laser wavelength at 300 mJ/cm^2 fluence, resulting in films with fluorescence spectra very similar to that of the bulk PVCz.

Allwood et al.[61] have reported on the growth of thin films of liquid crystal (LC) molecules by PLD at 308 nm. They deposited thin films of 5CB (4-cyano-4′-pentylbiphenyl) and of mixtures of other LC molecules using a 308 nm excimer laser under vacuum and at room temperature. For fluences in the range approximate to 30−100 mJ/cm^2 the films were found to have similar properties to that of the bulk material with no appreciable decomposition.

6.3.3. PLD of Composite Polymers

Gitay et al.[62] prepared composite films of polyimide−Sn by PLD of a segmented target containing Sn foils embedded in a polyimide matrix. The films were deposited at room temperature using a KrF excimer laser (248 nm). The resulting composite films contained clusters of Sn up to 2 μm in diameter uniformly distributed on a polyimide background. Such composite films comprising of a polymer and a high Z material could find uses as X-ray mask materials. Another example of PLD of composite films is provided by the work of Bubb et al.[63] They demonstrated the use of PLD to deposit electrically conductive polymer composites for chemical vapor sensing applications. Using a composite target consisting of ethylene vinyl acetate copolymer (EVA) mixed with 20% carbon powder by weight and using an ArF excimer laser (193 nm), the authors deposited 6 μm thick electrically conductive composite films on top of gold electrodes forming a type of chemical sensor known as a chemiresistor. The chemiresistors exhibited a reversible and fast (<1.3 s) response to toluene vapors. Moreover, the authors demonstrated that the performance of the chemiresistors fabricated from PLD films was significantly better than devices fabricated using more conventional polymer film growth techniques.

6.3.4. PLD of Biomaterials

Recently thin films of biomaterials such as enzymes and proteins have been deposited using PLD. These results are very relevant given the technological impact that thin films of biomaterials could have in novel areas such as bioelectronics, biosensors and biomedical applications.

In 1990 Nelson, et al. demonstrated that DNA molecules could be transferred from a frozen aqueous target intact by using pulsed laser energy with a matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) apparatus.[64] More recently, the group of Phadke and Agarwal[65] demonstrated the ability to deposit thin films of the enzyme glucose oxidase (GOD) dispersed in a sodium dodecylsulfate (SDS) matrix by PLD using a KrF excimer laser (248 nm) and also the third harmonic emission of a Nd:YAG laser (355 nm). The authors used a low concentration of GOD in SDS (1:500 molar ratio) to reduce the laser interaction with the protein and still allow the retention of the enzymatic activity of the GOD molecule. The resulting GOD-SDS films were subjected to various assays to determine the condition of the GOD component. The results indicated that the enzymatic activity of the GOD films grown by PLD was similar to that of the native enzyme. This approach, however, results in a contaminant-rich film that contains not only the enzyme of interest but also the surfactant used in the target. Using a similar setup, the authors also have shown the growth by PLD of thin films of preformed supramolecular assemblies of phospholipids incorporated with riboflavin (Rbf), a natural fluorophore.[66] They showed that the constituent molecules in the deposited material displayed characteristic native properties and the assemblies retained their morphological identity. In a following publication, the same authors reported the growth of supramolecular assemblies consisting of the photosensitive protein bacteriorhodhopsin (bR) embedded in the lipid L-α-phosphatidylcholine distearoyl (DSPC) by PLD.[67] Again the authors found that the structural and functional properties of the bR+DSPC assemblies were preserved by PLD.

Tsuboi et al. used PLD to deposit silk fibroin from a solid target onto quartz and ZnSe substrates in a vacuum.[68] They evaluated the properties of films deposited using two different excimer laser wavelengths (248 and 351 nm). The infrared spectrum of the deposited material was nearly identical to that of the bulk, pressed target material, for the films deposited at 351 nm, but a mass distribution of the deposited material was not reported. Furthermore, the secondary structures in the films were of the random coil type (amorphous), despite the fact that the targets consisted of antiparallel β-sheet type (crystalline) fibroin. In terms of applications of silk fibroin films for bio-electronic devices and biomedical implants, β-sheet type fibroin is preferred because of its insolubility. Later work by the same group demonstrated the ability to deposit silk fibroin protein films containing the β-sheet type structures by PLD using silk fibroin targets doped with anthracene (0.1−5 wt %) and either a XeF excimer laser (351 nm) or the third harmonic emission of a Nd:YAG laser (355 nm).[69] The anthracene was used to absorb most of the laser radiation, and convert it into thermal energy that caused the vaporization of the target without causing the excitation of the peptide chains (amino bonds) in the silk fibroin that result in the destruction of the β-sheet structure. For those samples deposited from targets containing the lowest anthracene concentration (0.1 wt %) and ablated at low laser fluences (0.55 mJ/cm^2), the highest fraction of β-sheet type structures was measured by FTIR analysis of the films. Table 4 provides a list of the aforementioned materials.

Table 4. List of Organic, Organometallic, Polymeric, and Biological Materials Deposited by PLD (Only the Wavelengths That Resulted in the Desired Film Are Listed)

polymer material	laser	comments	ref
fuchsine ($C_{20}H_{27}ClN_3$)	Ruby (694 nm)	room-temperature substrate	2
Ni-dimethyl glyoxime	Ruby (694 nm)	room-temperature substrate	2
poly(ethylene terephthalate)	ArF (193 nm), KrF (254 nm)	smooth films	16
polycarbonate	ArF (193 nm), KrF (254 nm)	smooth films	16
polyimide	ArF (193 nm), KrF (248 nm)	smooth films	16
	KrF (248 nm)	heated substrate	44
poly(methyl methacryalate) (PMMA)	ArF, KrF	smooth films (193 nm), rough films (248 nm)	16
	Nd:YAG (266 nm)	heated substrate	40, 41
nylon 6,6	ArF (193 nm), KrF (254 nm)	smooth films	16
polytetrafluorethylene (PTFE)	Nd:YAG (266 nm)	amorphous films	18
	Nd:YAG (266 nm)	mixed amorphous and crystalline films	20
	F_2 (157 nm)	crystalline films	28
	XeCl (308 nm) and CW CO_2 (10.6 μm)	amorphous films, CO_2 resulted on evaporation of PTFE	29
	KrF (248 nm)	crystalline films	30
	synchrotron radiation	crystalline films	31
poly(methylphenylsilane) (PMPS)	XeF (351 nm)	chemical decomposition	36
hexaphenyldisilane (HPDS)	KrF (248 nm)	chemical decomposition	37−39
polyvinylidene fluoride (PVDF)	KrF (248 nm)	heated substrates, amorphous films	27
polyphenylene sulfide (PPS)	KrF (248 nm)	heated substrates, crystalline films	43
polystyrene (PS)	XeF (351 nm)	target doped with anthracene	46
polyperinaphthalene (PPN)	Nd:YAG (266 nm)	amorphous films	47
	XeCl (308 nm)	perylenetetracarboxylic dianhydride target, heated substrate, crystalline films	48, 49
polyacrylonitrile (PAN)	XeCl (308 nm)	room-temperature substrate, crystalline films	50, 51
polyacenic semiconductive (PAS)	XeCl (308 nm)	phenol-formaldehyde target, heated substrate	52
polythiophene	KrF (248 nm)	laser chemical decomposition of 2,5-dichlorothiophene	53
copper phtholocyanine (CuPc)	KrF (248 nm)	pressed CuPc targets, amorphous films	54
	KrF (248 nm)	crystalline films with electrical bias of the substrate during deposition	55
aluminum tris-8-hydroxyquinline (Alq_3)	KrF (248 nm)	pressed Alq_3 targets	54
4-dialkylamino-4′-nitrostilbensen (DANS)	KrF (248 nm)	crystalline films with electrical bias of the substrate during deposition	55
poly(*p*-phenylenevinylene) (PPV)	Nd:YAG (355 nm)	room temperature	56
pentacene	KrF (248 nm)	deposited on heated substrates	57
	KrF (248 nm)	deposited at room temperature and on heated substrates	58, 59
poly(N-vinylcarbozole) (PVCz)	XeF (351 nm)	amorphous films, room temperature	60
5CB (4-cyano-4′-pentylbiphenyl) (liquid crystals)	XeCl (308 nm)	room temperature	61
polyimide/Sn composite	KrF (248 nm)	room temperature	62
ethylene vinyl acetate/ graphite composite	ArF (193 nm)	nanocomposite films	63
glucose oxidase (GOD)	KrF (248 nm) and Nd:YAG (355 nm)	low concentration GOD/SDS target (1:500 molar ratio)	65
silk fibroin	ArF (248 nm)	amorphous films	68
	XeF (351 nm)	crystalline films, target doped with 0.1 wt % anthracene	69

6.4. Summary of PLD of Polymers and Biomaterials

Despite the extensive list of polymer and biomaterials deposited by PLD presented in the previous sections, fundamentally the use of PLD for the deposition of organic and polymeric materials has provided mixed results at best. Moreover, despite the large number of variables explored in deposition parameter space by all the aforementioned groups, the quality of the films produced by PLD has only been optimal for a very small number of systems. By using a UV laser in order to ablate the various organic and polymeric targets, it is not surprising that the resulting films will tend to show some degree of irreversible decomposition or damage. Given the fact that in these materials the chemical bonds have energies well below the UV photon energies, some degree of photochemistry is expected to occur during the PLD process. Only for a small group of addition polymers such as PTFE, PMMA, etc., does the absorbed UV radiation cause photothermal depolymerization of the starting material resulting in the reversible unzipping of the polymer chains. More often than not, however, the interaction of the UV photons with the polymeric or organic molecules will

cause the loss or decomposition of functional groups, or in the case of condensation polymers, the resulting photochemistry will be responsible for the substantial modification of the starting material. Such modifications might be acceptable for some applications, but in general the use of lasers for depositing thin films of polymeric and biomaterials requires more subtle approaches than those offered by PLD alone.

7. MAPLE Deposition of Polymers and Biomaterials

The laser−material interaction and the subsequent relaxation of excitation is at the heart of laser-based film deposition techniques. Basically, there are only three possible ways to modify this, and that is by varying the laser or the material or both. For the approach described in this section, the composition of the target material is changed in a novel way in order to provide a softer desorption process

7.1. Fundamentals of the MAPLE Process

To minimize photochemical damage that results from direct interaction of the UV laser light with the organic or biomaterial target, a novel deposition technique, known as matrix-assisted pulsed laser evaporation (MAPLE), has recently been demonstrated at the Naval Research Laboratory.[70] The MAPLE technique has been used successfully to deposit thin and uniform layers of chemoselective polymers, as well as organic compounds such as simple carbohydrates and their polymers.[71] MAPLE is a variation of conventional PLD. It provides, however, a more gentle mechanism for transferring many different compounds that include small and large molecular weight species such as sugars and polymeric molecules, from the condensed phase into the vapor phase. In MAPLE, a frozen matrix consisting of a dilute solution (1−5%) of a polymeric compound 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.

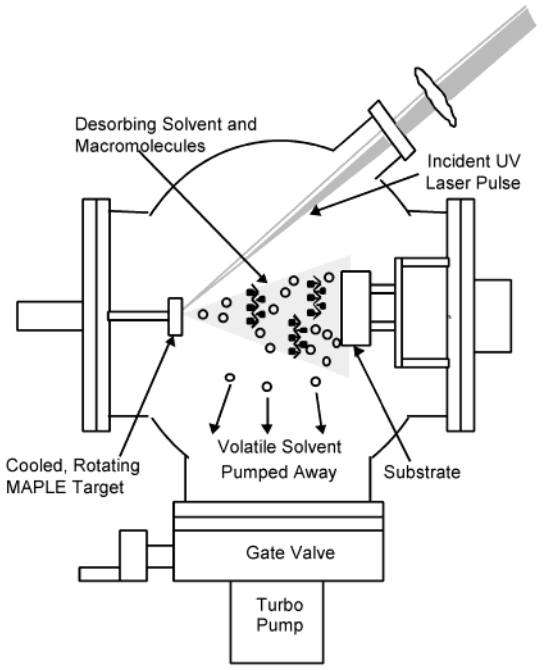

Figure 2. Schematic diagram showing the basic elements of a MAPLE deposition system.

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, which have very low sticking coefficients, are evacuated by the pump in the deposition chamber, as shown schematically in Figure 2. The MAPLE technique is analogous to the analytical technique matrix assisted laser desorption/ionization-mass spectrometry (MALDI-MS).[72] MALDI-MS is a soft ionization technique that allows the desorption and ionization of large molecular species (≈10−1000 kDa). This process has been developed for studying large organic molecules and polymeric materials to accurately determine their molecular weight distributions. The main difference between the MAPLE and MALDI techniques lies in the treatment of the evaporated polymer and in the selection of the matrix. In the MAPLE process, the polymer is not deliberately ionized and is collected on a substrate to form a coating rather than being directed into a mass spectrometer.

7.2. Polymeric Films by MAPLE

MAPLE was developed to overcome the difficulties in solvent-based coating technologies such as inhomogeneous films, inaccurate placement of material, and difficult or inaccurate thickness control. MAPLE is an extension of pulsed laser deposition (PLD), which often is unable to successfully form films of complex polymers or biomolecules due to photodecomposition. MAPLE is able to avoid this damage by embedding a polymer or biomolecule in a light-absorbent, high vapor pressure solvent. The resulting matrix preferentially absorbs the incident laser energy and the collective action of multiple collisions of the evaporating solvent with the embedded molecule result in a soft desorption with excellent struc-

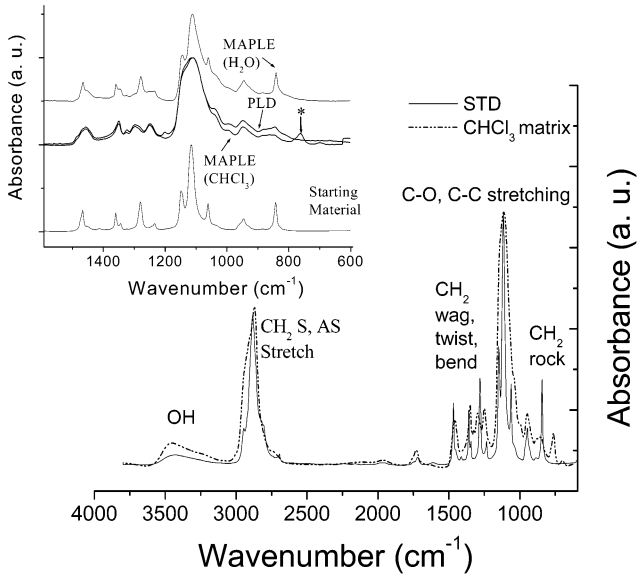

Figure 3. Infrared absorbance spectra for the MAPLE transfer of PEG films in a chloroform and water matrix and PEG films by PLD.

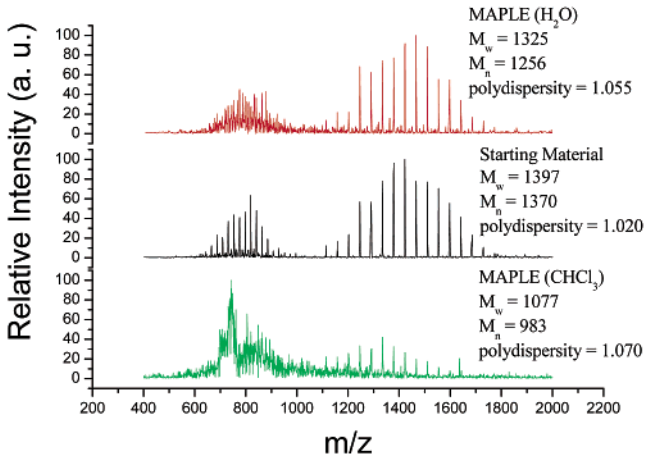

Figure 4. Mass distribution for the MAPLE transfer of PEG in a water matrix illustrating the nonreactive nature of some matrix−solute combinations.

tural fidelity. Several studies have investigated the MAPLE process under different conditions such as matrix concentration, type of matrix, laser energy, and laser wavelength.[73,74] In general, the results demonstrate that the material properties such as chemical structure and functionality depend strongly upon the laser wavelength, matrix, and energy used in the experiment. For example, photodecomposition of the matrix occurs when using some UV wavelengths and a chloroform matrix/solvent, resulting in reactive and destructive Cl free radicals formation. These radicals are found to chemically react with solute polymers such as poly(ethylene glycol) (PEG), resulting in degraded mass distributions of the deposited film (see Figure 3). However, with similar studies it has been shown that when a water matrix is used for PEG depositions, there are no reactive matrix species formed and molecular weight distributions are maintained when compared to the parent material (see Figure 4). These studies highlight the potential limitations with UV MAPLE experiments and have spurred studies of the MAPLE process using less energetic wavelengths such as infrared.

The original MAPLE studies were performed on polymer solutions with a specific interest toward depositing thin, homogeneous films of chemoselective polymers onto sensing platforms such as surface acoustic wave (SAW) devices. The requirements for thin film deposition onto these devices were not being met by traditional spray coating techniques, which left large areas of film inhomogeneities due to solvent drying effects. MAPLE deposited the same chemoselective agents without solvent effects because the process is pseudodry, eliminating the solvent during deposition by performing the experiments under vacuum. These films showed higher sensitivity and faster response times when challenged with various chemical vapors than their spray coated counterparts.[77] The initial experiments using the MAPLE technique focused on depositing a hydrogen bond acid functionalized polysiloxane known as SXFA.[70,77] To achieve the required sensor signal kinetics, it was required that the SXFA films were on the order of 10−50 nm thick and highly uniform across the whole area. Using the MAPLE technique, it was possible to demonstrate the deposition of such films on silicon substrates. AFM analysis of the MAPLE deposited SXFA films showed RMS surface roughness of the order of 3 nm.[70]

The MAPLE technique has also been used to successfully deposit thin films of organic molecules with a wide range of molecular weights using MAPLE thin films of various carbohydrates such as sucrose, glucose, and dextran were deposited.[71] Another biocompatible polymer that has been deposited by MAPLE is poly(ethylene glycol).[74] PEG has many biomedical applications that demand the preservation of its chemical structure during the deposition process.[84] The MAPLE technique has also been used to deposit composite polymer films. For example, polymer nanotube composite thin films have been grown by MAPLE using PEG as a polymer matrix.[78] The MAPLE process has also been used to deposit thin films of various electroptic polymers such as N-(4-nitrophenyl)-L-prolinol (NPP), polypyrrole, and Alq_3.[79] The MAPLE deposited NPP films showed optical absorptions similar to that of their bulk counterpart, while the polypyrrole films had electrical conductivities similar to polypyrrole films deposited by other techniques. In the case of the Alq_3 films, the MAPLE deposited samples exhibited optical absorption patterns different from those of bulk Alq_3, indicative of some decomposition that might have occurred during the MAPLE deposition process.[79]

7.3. Thin Biomaterial Films by MAPLE

The MAPLE process has also been successfully used in the growth of active protein thin films. Such films might play an important role in the development of next generation microfluidic biosensors and biochips, coating drug particles with functional (drugs, polymers, smart materials) films, microneedle coatings for various therapeutic applications (DNA vac-

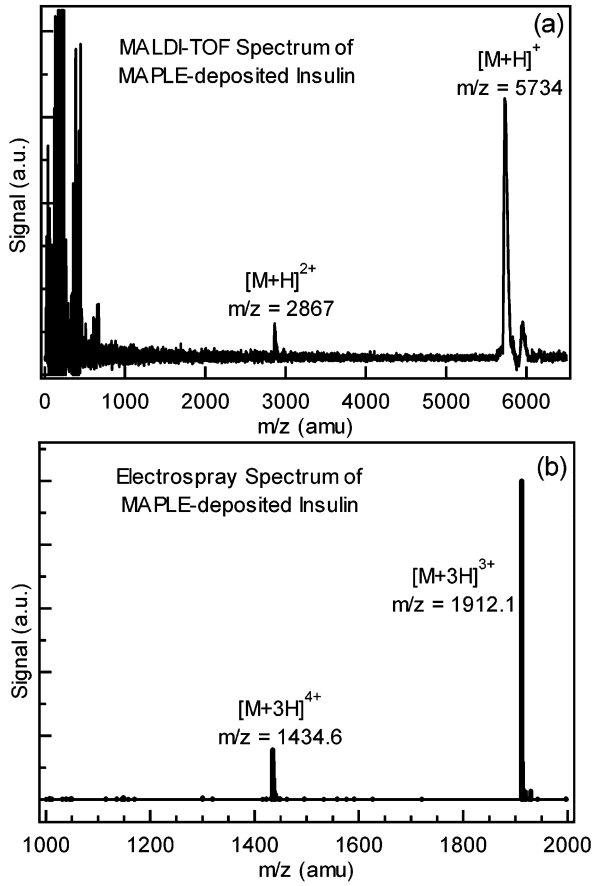

Figure 5. MALDI-TOF and ELISA-MS spectra for MAPLE-transferred insulin.

cines, gene therapy), coatings to prevent device failure due to biofouling, and biocompatible coatings for medical implants, just to name a few. Using the MAPLE technique, thin and uniform films of horseradish peroxidase (HRP) and insulin have been deposited on a variety of substrates such as Si, NaCl and gold and platinum coated Si.[80] Figure 5 summarizes MALDI-TOF and ELISA-MS studies on MAPLE-deposited insulin films that demonstrated near-intact transfer of this protein with little or no photoinitiated decomposition. Infrared spectra of the HRP films showed that the chemical and physical structure of the protein was maintained post-MAPLE transfer. A solvent-phase activity test performed on the HRP films also indicated that the majority of the transferred protein retains its chemical and physical structure as well as its biological activity. Specifically, Figure 6 shows a microarray of an HRP/polyurethane multilayered structure deposited through a shadow mask by MAPLE pictured before and after exposure to a DAB/H_2O_2 solution to test activity. Decomposition of DAB was observed (protein activity) for HRP spots with diameters as small as 50 μm (see dark brown material on/in HRP spots). These results represent the first demonstration that pure films of intact and active biomolecules can be deposited using a vapor-deposition technique. Additional studies have since been performed on other biomaterials such as 50/50 Poly(D,L-lactide-*co*-glycolide), biotinylated bovine serum albumin (BSA), and phospholipid polymers that also show maintained function and chemical structure in the thin films.[81]

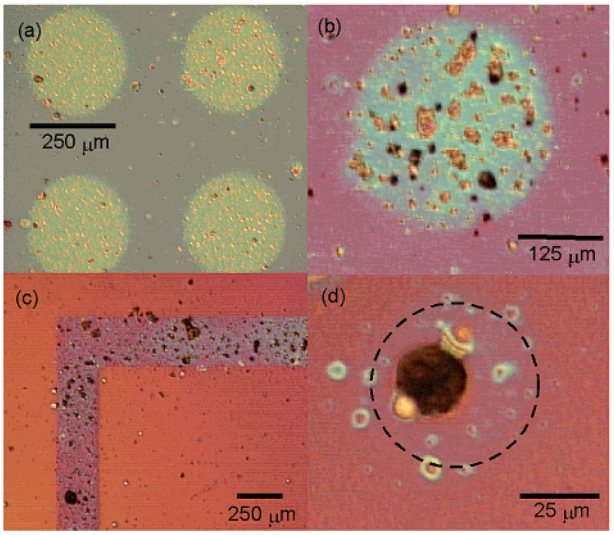

Figure 6. Microarray of an HRP/polyurethane multilayered structure deposited by MAPLE through a shadow mask before and after exposure to a DAB/H_2O_2 to test activity.

Current studies are focused on applying MAPLE to biomolecules that are used in biosensors with the goal of fabricating a functioning chip-scale device. There are plans to explore the extent to which MAPLE can be used to transfer different biomolecules such as DNA or antibodies perhaps investigating how different wavelengths such as IR change film qualities. The current studies also highlight the need for further investigations to determine the best methods to adhere MAPLE-deposited biomolecules to different surfaces without perturbing their activity. Current efforts directed toward the creation of polymer-protein composites to increase adhesion have been successful, but patterning such composite materials has produced particulate-rich films. To mitigate this effect, methods are being explored to modify the substrate surface to increase material adhesion as well as to chemically immobilize deposited molecules in situ. MAPLE also holds potential to deposit not only biomolecules but also a matrix that acts to maintain the activity of the sensitive material or help adhere it to the substrate. Overall, MAPLE holds promise as a novel and versatile technique to deposit and pattern thin, active biomolecular films of varying thickness and surface morphologies.

7.4. MAPLE Summary

The above discussion highlighted several attributes of the MAPLE technique for depositing organic, polymeric, and biomaterial thin films, and a summary of the conditions for some of the materials successfully deposited by MAPLE is given in Table 5. MAPLE is capable of forming thin films over a wide range of thicknesses from 10 nm to over 1 μm and with accurate thickness control (<0.05 nm/laser shot). Many current technologies using SAMs are only capable of depositing monolayers, while other thick film deposition techniques, such as ink jet printing, are unable to control thickness and film uniformity. MAPLE's thickness control and accurate material placement, therefore, may be particularly

Table 5. Summary of Deposition Conditions for the Various Materials Successfully Deposited Using the MAPLE Technique

material	solvent matrix	solute concentration (w.t. %)	laser wavelength (nm)	laser fluence (J/cm^2)	background gas and pressure (Torr)	ref
fluoroalcoholpolysiloxane (SXFA)	*tert*-butyl alcohol	0.5	248	0.05	Ar @ 5×10^{-2}	70
glucose	H_2O	5	193	0.1	Ar (saturated with H_sO) @ 5×10^{-2}	71
dextran	H_2O	5	193	0.1	Ar (saturated with H_sO) @ 5×10^{-2}	71
poly(ethylene glycol)	H_2O	2	193	0.2	none @ 5×10^{-6}	74
carbon nanotube/poly(ethylene glycol) composite	$CHCl_3$	N/A	248 or 193	0.2	Ar @ 5×10^{-2}	78
insulin	phosphate buffer solution	0.5	193	0.2	none @ 5×10^{-5}	80
horseradish peroxidase	phosphate buffer solution	0.5	193	0.2	none @ 5×10^{-5}	80

useful for thick film amperometric biosensors where accurate thickness control and uniform film coverage are crucial to signal output. The surface morphology of the films can also be controlled by MAPLE, enabling this technique to tune the roughness of films to meet specific device requirements. Multilayers of many different materials (i.e., polymers, active biomolecules) can also be formed in situ, enabling protective overcoats or membranes to be easily formed. In addition, co-depositions can be performed by using multicomponent targets with proteins or DNA combined with polymers or other functional materials to aid in stability, adhesion onto nontraditional surfaces, or molecular activity. By using MAPLE and PLD together, laser-based techniques could sequentially deposit electrodes, active biological molecules, and a polymer or biomaterial coating to immobilize and protect the underlying materials. Multiple materials can also be patterned adjacently on the same substrate, enabling microarrays to be fabricated with feature size and spacing as small as 20 μm. MAPLE is unique because it is able to combine these attributes into one processing tool to fabricate structures unattainable by other technologies.

8. Resonant IR Deposition of Polymers and Biomaterials

Resonant infrared pulsed laser deposition (RIR-PLD) is a variant on 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 (Figure 7). So far, this approach has been used with polymers in the mid-infrared wavelength range (2−10 μm). The use of a UV laser, as in conventional PLD, typically results in direct dissociative photochemical reactions when the target material contains strongly UV-absorbing moieties. The best that one can hope for, as in the work of Blanchet et al.,[18−20] is for the absorbed radiation to result in photothermal depolymerization of the target material, with subsequent repolymerization at the substrate. However, if the degree of repolymerization is incomplete, such as

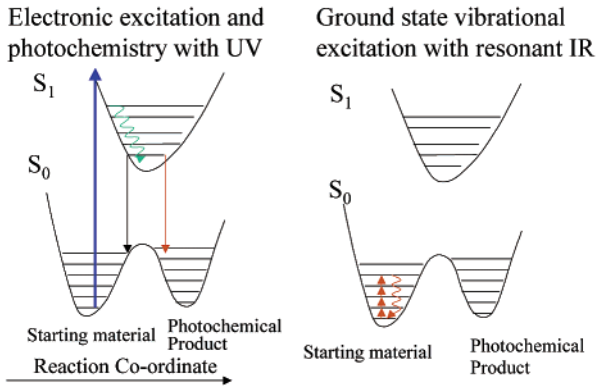

Figure 7. Energy level diagrams showing the difference between electronic excitation and photochemistry with UV radiation and ground state vibrational excitation with resonant IR radiation in terms of producing different photochemical products.

when a photochemical reaction causes the loss of a pendant functional group, or in the case of condensation polymers or copolymers, the polymer will be subject to substantial modification in comparison with the bulk starting material. Therefore, UV-PLD is useful for only a small class of polymers such as addition polymers that do not have strong UV-absorbing moieties, or in applications when it is acceptable to modify the polymer substantially without loss of functionality.[63]

8.1. RIR-PLD of PEG

Extensive studies have been carried out with RIR-PLD of poly(ethylene glycol) (PEG).[82,83] PEG is a technologically important polymer with biomedical applications.[84] Examples include tissue engineering,[85] spatial patterning of cells,[86,87] drug delivery coatings,[88,89] and anti-fouling coatings.[90] In addition, PEG is a mass spectroscopic standard for such techniques as electrospray ionization mass spectroscopy (ESI),[91] MALDI,[92] and gel permeation chromatography (GPC).[93] There are certainly application for which it is acceptable to deposit chemically modified PEG polymeric material;[87,94] however, in drug delivery and in vivo applications, it is important that there is no difference in the chemical and structural properties of PEG films compared with the bulk polymer.

The fact that PEG is a mass spectroscopic standard facilitates the characterization of the deposited thin films. Typically, to characterize the films, Fourier

transform infrared spectroscopy (FTIR) is used in conjunction with one of the mass spectroscopic techniques listed above. It is important to note that the information gleaned from FTIR measurements is primarily indicative of the properties of the basic repeat unit. This has little, if anything, to do with the molecular weight of the films. Small changes in the mid-infrared absorbance either due to new or missing bands reflect significant rearrangement of the polymer. Since the basic chemical structure of the coating polymer is altered, FTIR and GPC, ESI, or MALDI may not be reliable for characterization and process monitoring, since one is not comparing starting material with processed material, but rather trying to characterize an unknown. Therefore, it is important to carefully compare both the mid-infrared absorbance spectra of the bulk starting material and the deposited films along with molecular weight distributions. This comparison is most meaningful when the mid-infrared spectra are nearly identical, as the assignment of the mass peaks will depend on the chemical structure of the molecule.

The light source used for most of the experiments involving RIR-PLD of polymer films was an rf-linac-driven free-electron laser (FEL) at the W. M. Keck Foundation Free-Electron Laser Center at Vanderbilt University. The FEL generates light from a high-brightness beam of relativistic electrons by passing them through a spatially periodic magnetic field.[95] The Vanderbilt FEL produces a 4 μs macropulse at a repetition rate of 30 Hz; the macropulse in turn is comprised of approximately 11 400 1-ps micropulses separated by 350 ps.[96] The energy in each macropulse is of order 10 μJ, so that the peak unfocused power in each micropulse is very high. Unlike conventional lasers, the relevant intensity is that of the micropulses, which remains constant over the macropulse; the FEL fluence, on the other hand, is controlled by the duration of the macropulse. The average power of the FEL is of order 2−3 W. The FEL is also continuously tunable over the range 2−10 μm. In general, FEL's have a remarkable array of capabilities and applications.[97]

In a direct comparison of UV-PLD and RIR-PLD of PEG, it was found that when the laser was tuned to a vibrational resonance (i.e. 2.90 μm for OH stretch), it was possible to deposit thin films which were nearly identical to the starting material.[82] In contrast, the films deposited using an ArF UV laser (λ = 193 nm), show substantial photochemical and/or photothermal modification. In Figure 8, the mid-infrared absorbance spectra of an UV-PLD film, a RIR-PLD film, and the starting material are compared. There is excellent agreement in the position and intensity of bands for the RIR-PLD film and the starting material. In contrast, in the spectrum of the UV-PLD film, there are substantial differences in both the position and intensity of bands in comparison with the starting material. The differences are such that it would be more correct to refer to this material as 'PEG-like' rather than PEG.

Figure 9 displays the ESI mass spectra of the starting material and UV- and RIR-PLD films. Clearly, there are significant differences in the mass

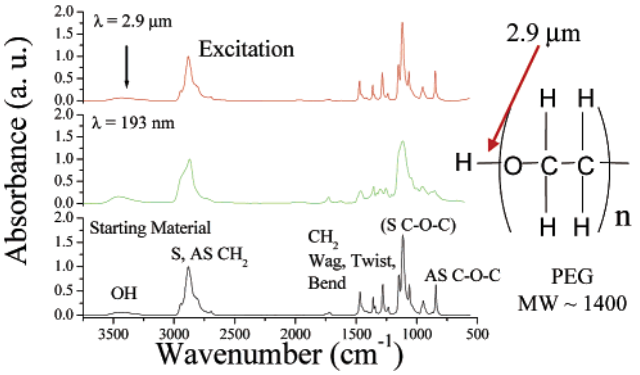

Figure 8. Infrared absorbance spectra for a UV-PLD film, an RIR-PLD film, and the starting material.

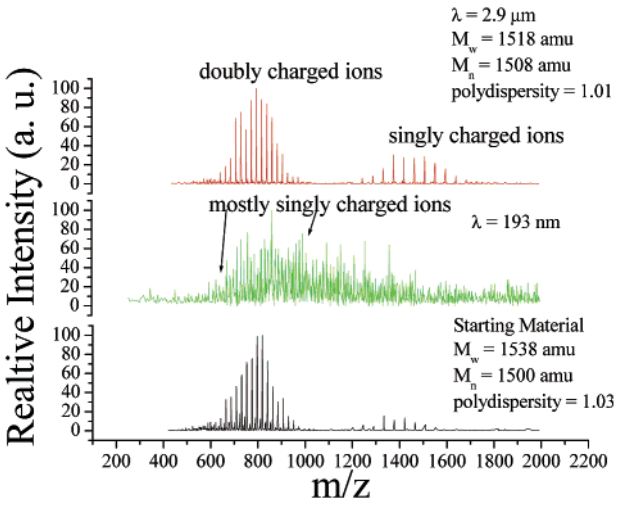

Figure 9. ESI mass spectra of the starting PEG material and UV-PLD and RIR-PLD deposited PEG films.

spectra of the UV-PLD film and the starting material, while the RIR-PLD film's mass spectra closely resembles the starting material. The position and intensity of the ion peaks in the mass spectrum of the UV-PLD film are unrecognizable. It is important to note that the concentration of the solutions that are injected into the ESI time-of-flight mass spectrometer are the same in all cases. Although the UV-PLD film's spectrum appears like noise, the peaks are real. The pattern displayed does not register in any meaningful way with the starting material, so the film deposited by UV-PLD is once again "PEG-like," while the RIR-PLD film is PEG.

Further studies[83] have demonstrated the importance of resonant excitation. It is not enough to tune the laser to a wavelength that does not cause electronic excitation, the target material must resonantly absorb the light. For PEG, films can be deposited using off resonant light; however, they show substantial chemical and structural modification, as in the case of UV-PLD. In Figure 10, we display the mid-infrared absorbance of a film deposited using both resonant (3.3 μm) and nonresonant (3.4 μm) light. The film deposited with nonresonant light has substantial modification in the fingerprint region of the absorbance spectrum. The mass distributions of films deposited using nonresonant light are similarly affected.

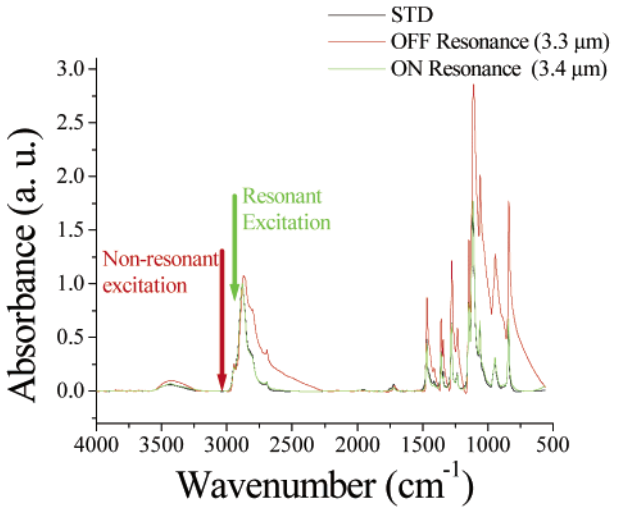

Figure 10. Infrared absorbance spectra for the PEG standard and resonant and nonresonant PLD film.

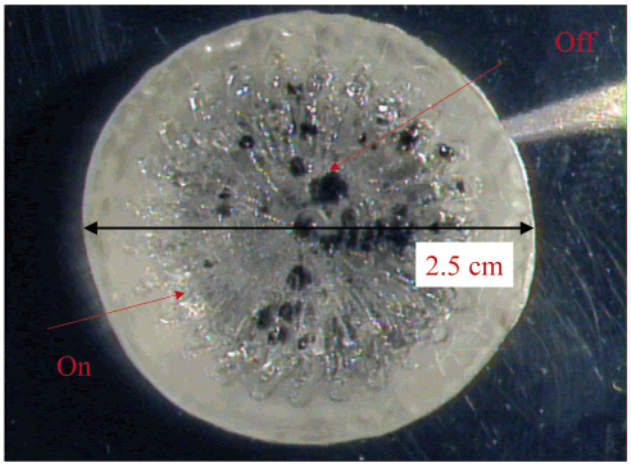

Figure 11. Optical micrograph of a target that has been irradiated with both resonant and nonresonant IR radiation.

8.2. Other Systems Deposited by RIR-PLD

In contrast, in RIR-PLD experiments with polystyrene, it was not possible to deposit a film using off resonant radiation in the fluence range investigated.[98] In this case, off resonant irradiation resulted in charring of the target and the creation of subsurface defects. In Figure 11, an optical micrograph is displayed which has been irradiated with both resonant (3.28, 3.30 μm) and nonresonant (2.90 μm) light. The blackened areas are defects created by the laser.

In addressing the mechanism of ablation, one typically compares the optical penetration depth $l_p \sim 1/\alpha$ and the thermal diffusion length $l_t = \sqrt{D_t \tau}$, where α is the absorption coefficient, τ is the macropulse length, and D_t is the thermal diffusivity. The thermal diffusivity of many polymers is around 0.001 cm^2/s at 300 K.[99] For polystyrene, at the wavelengths used, $\alpha \sim 1000$ cm^{-1}, and for PEG, $\alpha \sim 100-2500$ cm^{-1}. Therefore, these polymers have optical penetration depths of about 4−100 μm and thermal diffusion lengths of about 700−1000 nm.

This is indicative that RIR-PLD occurs in the weak thermal confinement regime in which ablation occurs by spallation. However, given that at high fluence, weak visible emission can be observed,[98] it seems more likely that nonlinear absorption is occurring and this may reduce the penetration depth substantially. This could even result in moderate to strong thermal confinement where substantial fractions of the laser energy are transferred to the kinetic energy of large molecules or even liquid droplets, with less into potentially destructive internal excitations. Further studies will be necessary in order to ascertain how much nonlinear absorption might contribute to the density of vibrational excitation.

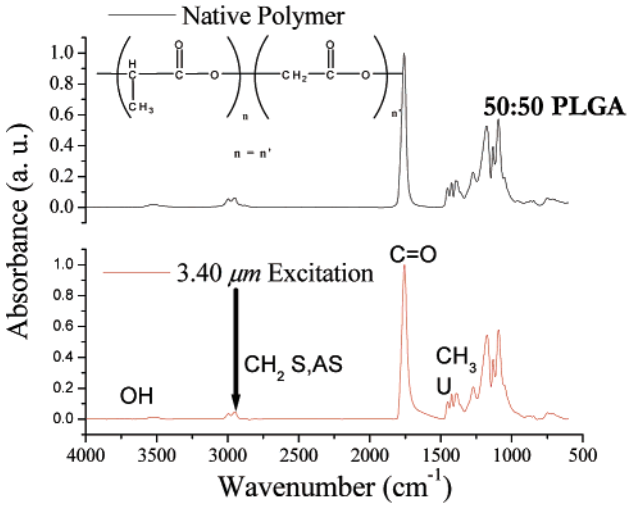

Figure 12. Infrared absorbance spectra for the standard PLGA and the RIR-PLD deposited film excited with 3.4 μm radiation.

8.3. Future Directions

RIR-PLD has the potential to have a dramatic impact on several application areas. Among these are chemical sensing and drug delivery coatings. Because it is a vapor deposition technique, PLD can be used to coat nonplanar substrates such as drug particles and implant devices.[100] However, many of these polymers are thermally sensitive and/or susceptible to photochemical interactions. One example is poly(DL-lactide co-glycolide) (PLGA), a copolymer used in drug release formulations. RIR-PLD has been used to deposit PLGA (Figure 12).[120]

Chemical and biological sensing are additional areas of application on which RIR-PLD is expected to make a significant impact. A common architecture for chemical sensors utilizes a polymer film deposited on an active substrate. Through sorption processes, the polymer film interacts with the analyte and swells. This swelling can be detected through electrical, mechanical, or optical means. For optimum sensitivity and reproducibility, uniform films are required. Recently, RIR-PLD has been used in order to deposit fluoropolyol,[101] a sorbent, chemoselective oligomer.[102] The results show that RIR-PLD is capable of transferring structurally sensitive materials without modification of either the chemical structure or the molecular weight distribution. Many of the polymers that are useful in chemical sensing applications will not tolerate mild decomposition without losing functionality both chemically and as sensor materials. Figure 13 displays a pictorial representa-

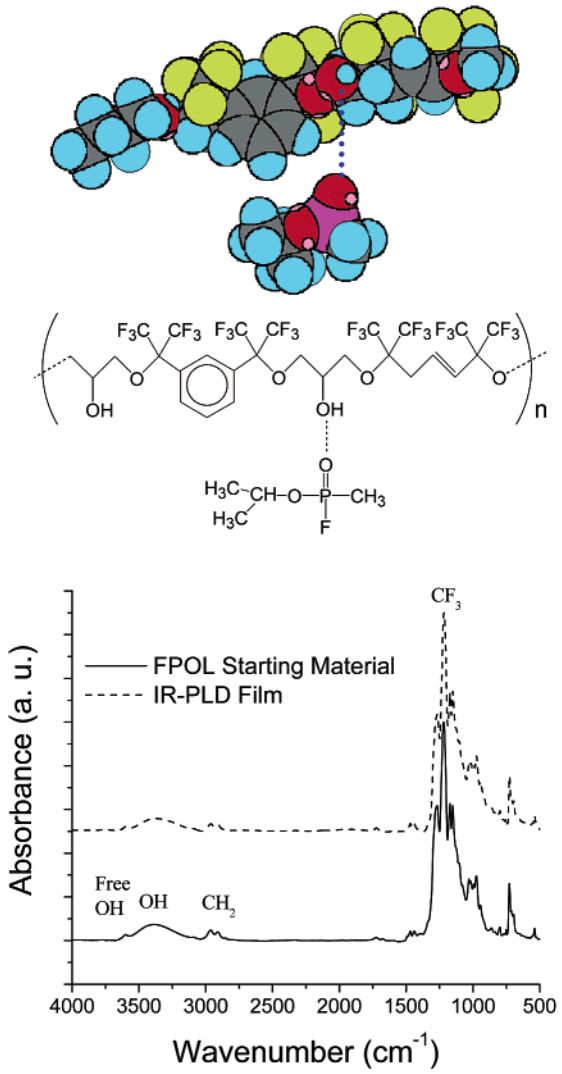

Figure 13. Pictorial representation of one repeat unit of FPOL and the infrared absorbance spectra for the FPOL starting material and the RIR-PLD deposited film.

tion of one repeat unit of fluoropolyol interacting with GB-Sarin a deadly nerve agent and compares the infrared spectrum of the deposited film with the starting material. The power of RIR-PLD is clear in this figure as the deposited film is identical to the starting material. A summary of the conditions for some of the materials successfully deposited by RIR-PLD is given in Table 6.

9. Laser Forward Transfer of Polymers and Biomaterials

9.1. Introduction

All previous sections describe somewhat traditional forms of laser processing in that they follow the model of PLD, i.e., laser/target interaction produce a plume of material that is then deposited onto a substrate in thin film form. Several groups around the world are beginning to use lasers in completely new ways to directly deposit 2-D and 3-D patterns and structures of tremendously diverse materials such as inorganics, polymers, biomolecules, and even living cells. These techniques can be broadly classified as laser forward transfer techniques, many of which are referred to as direct-write technologies because of their ability to form patterns without the aid of lithographic tools such as masks or molds and all under ambient conditions. With their unique ability to rapidly and serially deposit multilayers of inorganic, polymeric, and biological materials onto virtually any substrate, these techniques hold promise to make significant contributions across many scientific disciplines ranging from tissue engineering to electronics.

9.2. Organic Molecules and Polymeric Materials

There are two major groups working on the deposition of organic and polymeric materials with laser forward transfer techniques. The first is H. Fuku-

Table 6. Summary of the Deposition Conditions for Materials Sucessfully Deposited by RIR-PLD

polymer target[a]	wavelength	IR spectra (yes = good agreement between film and target)	MW by EI/MS (target) (nm = not measured)	MW by GPC (target) (nm = not measured)	ref
poly(ethylene glycol)	resonant (2.90 μm (O−H) 3.40 μm (C−H), 3.45 μm (C−H), 8.96 μm (C−O) and nonresonant (3.30, 3.92, 4.17 μm)	yes	MW ∼ 1500 @ 2.9 μm (1500)	MW ∼ 1500 @ 2.9 μm (1500)	82
polystyrene	3.42, 3.48, 3.28, 3.3 (C−H)	yes	nm	MW ∼ 25775 ± 3000 g/mol (∼322000) @ 3.42 μm, MW ∼ 25400 ± 1000 g/mol (∼322000) @ 3.48 μm	98
fluoropolyol	2.9 μm (O−H)	yes	nm	2398 (∼2400) @ 2.9 μm	102
PLGA (50−50)	2.90 μm (O−H) and 3.40 μm (C−H)	yes	nm	3125 (8495) @ 2.90 μm, 3470 (8495) @ 3.40 μm	120

RIR-PLD Conditions

laser (free electron laser at Vanderbilt University)	deposition chamber
macropulse repetition rate = 30 Hz	base pressure ∼ 10^{-4} to 10^{-6} Torr
macropulse energy: 10−30 mJ/pulse (∼ 4 μs wide)	deposition pressure ∼ 10^{-3} Torr
spot size: 0.005−0.03 cm^2	target substrate distance 3−4.6 cm
macropulse fluence: 1−20 J/cm^2	deposition rate ∼ 10 ng cm^{-2} macropulse^{-1}
micropulse fluence: 0.87−1.75 mJ/cm^2 (1 ps wide, 350 ps spacing)	

[a] Deposition time, typically 5−8 min for ∼ 0.5 μm thick film. All 100% polymer targets.

mura's group at Osaka University and most recently at Tohoku University that has performed several experiments to deposit organic molecules onto polymer surfaces using a technique termed laser molecular implantation (LMI).[103−109] The other group is at the Naval Research Laboratory, where they have deposited patterns of a wide range of organics such as polymer−carbon and inorganic/organic composites using a technique referred to as MAPLE direct-write.

9.2.1. Laser Molecular Implantation (LMI)

LMI has been used to deposit patterns of a large range of organic molecules onto and into polymer surfaces. Examples include the implantation of pyrene into PMMA films, implantation of other fluorescent molecules such as diphenyl antrhacene (DPA) into polybuthylmethacryalate or PBMA films, and implantation of photochromic molecules into various polymer films in an attempt to form devices such as diffraction gratings, optical switches and rewritable memories.[103−109] Initially, the authors used a PMMA matrix containing 2.5−3.5 wt % pyrene, and applied it to a ribbon by spin coating. They then transfer the pyrene from the ribbon onto a PMMA film in contact with the ribbon via laser irradiation. Utilizing novel materials as propellants has made further improvements to this technique.[110] More recent studies have expanded to experiment on the laser generation of nanojets for direct-write of organic molecules. This technique has been used to deposit submicron patterns of organic molecules onto polymer films as well as nontraditional substrates such as chicken skin.[111−116]

9.2.2. Matrix-Assisted Pulsed Laser Evaporation Direct-Write (MAPLE DW)

MAPLE DW was originally developed as a method to rapidly prototype mesoscopic passive electronic devices such as interconnects, resistors, and capacitors.[117,118] This technology falls under the category of a "direct-write" approach because, in the same manner as a pen or pencil, it can be used to rapidly form any pattern with the aid of CAD/CAM systems. The schematic of the apparatus is shown in Figure 14. The material to be transferred is mixed in a laser−absorbent matrix and coated onto a support, or ribbon, that is transparent to the laser irradiation. A focused laser pulse is directed through the backside of the ribbon so that the laser energy first interacts with the matrix at the ribbon interface. The laser pulse is focused at the matrix-ribbon interface by a UV microscope objective that also serves as an optical guide to determine the area of the matrix to transfer. Layers of matrix near the support interface evaporate due to localized heating from electronic and vibrational excitation. This sublimation releases the remaining material further from the interface by gently and uniformly propelling it away from the quartz support to a substrate positioned 25 μm to several mm away. By removing the ribbon and allowing the laser pulse to interact with the substrate, this approach is also able to micromachine channels and through vias into polymer, semiconductor, and metal surfaces. All micromachining and material transfer

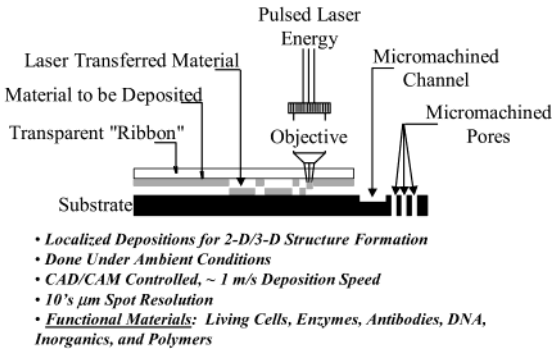

Figure 14. Schematic diagram of a MAPLE DW deposition system.

can be controlled by computer (CAD/CAM), which enables this tool to rapidly fabricate complex structures without the aid of masks or moulds.

When applied to polymers and composites, MAPLE DW has produced 2-D and 3-D patterns as well as functioning devices. One such device was a chemoresistor fabricated by depositing a polymer/carbon composite (polyepichlorohydrin/graphite mixture) across two electrodes.[117] This device retained function as demonstrated by sensitivity to chemical threats. In addition, polymer thick film (PTF) resistors were fabricated using epoxy-based materials.[121] The fabricated PTF resistors spanned four decades of sheet resistances (10 Ω/sq. to 100 k Ω/sq.) and performed consistent to theoretical models for temperature and frequency variance.

9.3. Living Cells and Biomolecules

9.3.1. Introduction

Methods to generate mesoscopic patterns of viable cells and active biomaterials are required to fabricate next generation cell, protein, or antibody-based microfluidic biosensors, tissue constructs engineered cell-by-cell, as well as high throughput gene and protein recognition microarrays.[122−129] These applications also often require biomaterials to be placed onto electronic circuits or other detection devices, producing interfaces between abiotic and biotic materials. At present there are several technologies capable of writing adjacent patterns or three-dimensional structures of different biomaterials, but fewer techniques exist that produce patterns that are software generated, have micron resolution and are written at submillisecond times. Two laser-based direct-write techniques (MAPLE DW and Laser Guidance Direct-Write) have been developed that are capable of forming patterns and 3-D structures of living cells and active biomaterials with resolution of less than 10 μm.[130,131] These laser transfer techniques are also capable of forming interfaces between biological and electronic materials by forming patterns of biotic (living microorganisms, active proteins, enzymes, DNA, antibodies, etc.) and abiotic (passive electronic devices and other inorganics such as phosphors) material adjacently on the same substrate or in multilayers.[117,118,132] Representative experiments will be described below for biomaterial structures formed by both these laser-based direct-write techniques.

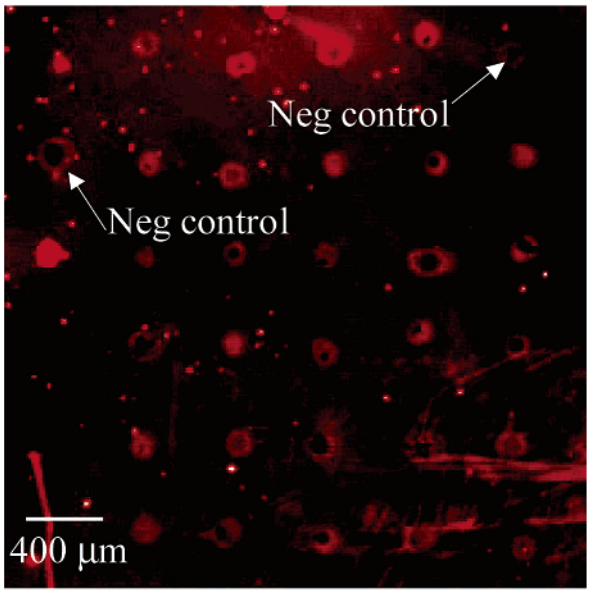

Figure 15. Fluorescent micrograph of a 6 × 6 microarray of different antibodies specific to several classes of cell-signaling proteins.

9.3.2. MAPLE DW

MAPLE DW has successfully transferred solutions or suspensions of several active proteins including a dopamine-sensitive enzyme (PPO),[133] biotinylated bovine serum albumin, anti-BSA,[134] and several antibodies specific to proteins involved in cell signaling pathways. Our most recent results are focused toward the fabrication of a multi-antibody microarray that could be used both for sensing of biological warfare agents and early detection of diseased states through protein screening and identification. Pictured in Figure 15 is a fluorescent micrograph of a 6 × 6 microarray of different antibodies specific to several classes of cell-signaling proteins deposited onto a nitrocellulose-coated glass slide by MAPLE DW. The microarray has been treated with cacein to block all areas of the array not containing active elements and was then exposed to a solution of fluorescently tagged proteins derived from a osteoblast culture with no alterations to the signaling pathways. Fluorescence is observed for nearly every spot when the protein-exposed microarray is viewed under UV exposure. This result indicates the activity of MAPLE DW deposited proteins is high, enabling antibody−protein binding and fluorescent imaging with high signal-to-noise ratios. In addition, the efficiency of the MAPLE DW process for depositing protein solutions is very high due to the small volume dispensed (<10 pL/drop) and small volume of starting material required (<500 nL). Compared to traditional protein dispensing techniques such as pin arrayers, quill-pin arrayers, and ink jets, MAPLE DW's capabilities in terms of spot size, speed (∼ 1m/s linear travel), and efficient use of material surpass current state-of-the-art.

MAPLE DW has also formed patterns and structures of living cells by optically selecting a group of cells from culture and using the pulsed laser to actuate the transfer to a separate substrate. This

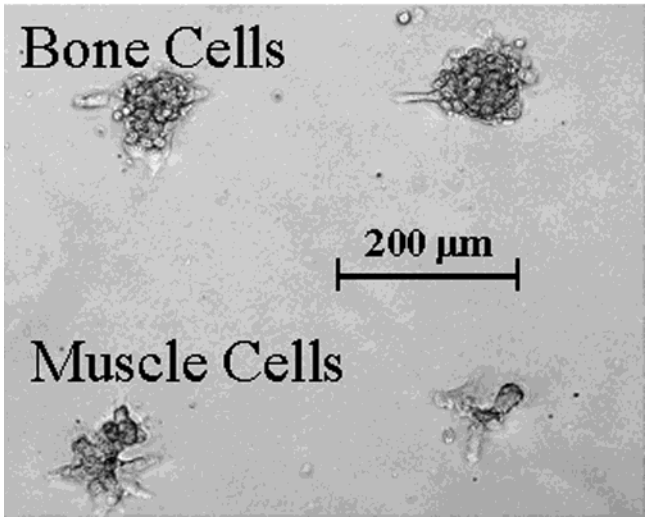

Figure 16. Example of a multicell type array deposited by MAPLE DW. Rat cardiac cells and human osteoblasts were deposited adjacent to each other.

transfer effectively "punches out" a group of cells from a sustained culture, placing this small, dissected subculture over areas as small as 50 μm in a new environment or substrate. Both eukaryotic and prokaryotic cell patterns have been formed with near 100% viability demonstrated via standard live/dead assays and green fluorescent protein marking.[133,135] Recently, MAPLE DW has been used to successfully deposit patterns of a broad range of cell types including *E. coli*, chinese hamster ovaries, human osteoblasts, mouse pluripotent cells, and mouse myoblasts. Figure 16 is an example of a multicell type array deposited by MAPLE DW. Rat cardiac cells and human osteoblasts were deposited adjacent to each other in a 2 × 2 microarray. The cells were immediately submerged in growth media and allowed to grow for 24 h post-transfer. The image shown in Figure 16 was taken after this growth period and demonstrates pseudopod extension and obvious cell viability. Current studies are underway to use surface antigen probes to distinguish different cell types adjacent to one another, while other continuing studies are aimed at building living tissue from its basic components. MAPLE DW presents the possibility of a tool to manipulate cells and biomolecules into ordered structures, potentially mimicking the natural structure and composition of living tissue.

We have also used MAPLE DW to transfer biomaterials from pathologic tissue.[81] A 5 μm and 200 μm × 150 μm oval structure prostate tissue array has been fabricated, see Figure 17. The ribbon for the MAPLE DW tissue transfers is made by first coating a quartz plate with gelatin. A thin tissue section is then layered on top of this gelatin layer, which effectively is an absorption region that protects the overlaid tissue and acts as a propellant to release the tissue to the receiving substrate. Figure 17 shows an array of prostate tissue "discs" in paraffin deposited on a glass slide. Each disk represents a single laser shot, transferring blocks of tissue quickly and easily. We have also performed experiments that suggest that cell structure may be maintained. These representative examples are indicative of the MAPLE DW

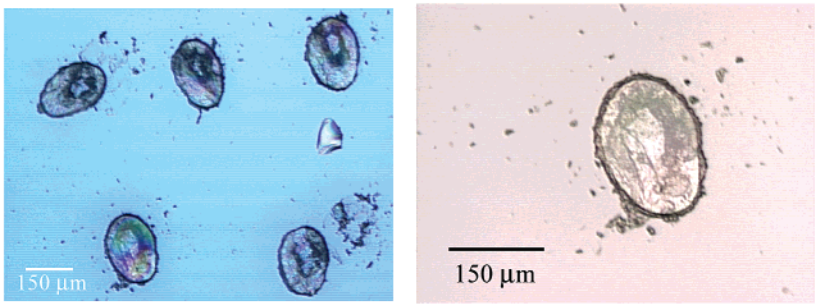

Figure 17. Oval-shaped piece of prostate tissue (200 μm × 150 μm, 5 μm thick) transferred by MAPLE DW.

process which is a tremendously versatile technique to process many different classes of materials into functional patterns, structures, or devices.

9.3.3. Laser Guidance Direct-Write

Laser guidance direct-write uses physical forces produced by laser irradiation to control and direct different materials down a hollow fiber. By moving a substrate beneath this fiber, patterns of the various materials can be made in a CAD/CAM controlled fashion. When the light from a near-infrared diode laser focused through a low numerical aperture lens, individual embryonic chick spinal cord cells can be guided through culture medium and deposited on a glass surface to form smart clusters of cells.[136] Cell viability was verified by observation of normal cell adhesion and neurite outgrowth post-laser exposure. Similar to MAPLE DW, this laser-based direct-write technique holds promise to deposit complex, adjacent patterns of different cell and biomaterials on the same substrate.

9.3.4. Future Directions

Potentially the greatest advancement that these laser-based tools provide for biotechnology is their ability to weave together the electronic and biological worlds. One of the advances that will be derived from biotechnology will be the routine use of the "biochip", defined as a miniature device designed to detect changes in biological systems. The potential of biochips ranges from high throughput screening for genomics and proteomics to DNA separations and cell-based reactions performed on a laboratory the size of a fingertip. To gather data (signal transduction), these systems often require electronic, polymeric, and biological elements, each of which can be processed by laser-based tools. For example, MAPLE and MAPLE DW are capable of forming patterns and multilayers of electronic devices, polymers, and biological materials. Therefore, each of these tools could be used in a serial fashion to fabricate the components necessary to build improved biochips.

These new laser-based tools exemplify the progress that can be made when physical and biological sciences are interwoven together with engineering. By breaking down the traditional barriers between the physical and life sciences, new technologies can be developed that create working solutions to current and future problems. With the ability to accurately and uniformly deposit a variety of technologically important materials, novel laser-based tools should contribute to the continuous process of taking biotechnology from the laboratory into the marketplace.

10. Summary

This article has shown the wide range of possible laser−material interactions and that under the right combination, pulsed laser processing of organic and biological thin film materials offers many of the qualities of a generic physical vapor deposition technique with added finesse. Lasers can be used to process a wide range of materials with significant control of quality and thickness. Techniques such as matrix assisted pulsed laser evaporation (MAPLE), MAPLE direct-write, and resonant infrared pulsed laser deposition (RIR-PLD) can produce high-quality films from relatively simple carbohydrates to complex systems such as living cellular materials.

11. References

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