Resonant infrared pulsed laser deposition of a polyimide precursor

N L Dygert, K E Schriver and R F Haglund, Jr
Department of Physics and Astronomy and W M Keck Foundation Free-Electron Laser Centre, Vanderbilt University, Nashville TN 37235 USA
Email: nicole.l.dygert@vanderbilt.edu

Abstract. Poly(amic acid) (PAA), a precursor to polyimide, was successfully deposited on substrates without reaching curing temperature, by resonant infrared pulsed laser ablation. The PAA was prepared by dissolving pyromellitic dianhydride and 4, 4’ oxidianiline in the polar solvent N-methyl pyrrolidinone (NMP). The PAA was deposited in droplet-like morphologies when ablation occurred in air, and in string-like moieties in the case of ablation in vacuum. In the as-deposited condition, the PAA was easily removed by washing with NMP; however, once cured thermally for thirty minutes, the PAA hardened, indicating the expected thermosetting property. Plume shadowgraphy showed very clear contrasts in the ablation mechanism between ablation of the solvent alone and the ablation of the PAA, even at low concentrations. A Wavelength dependence in plume velocity was also observed.

1. Introduction
Polymer thin films are now widely used in sophisticated optical, electronic, and medical technologies ranging from micro-electro-mechanical systems (MEMS) to polymer light-emitting diodes (PLEDs) and drug-delivery coatings. In many applications, device functionality requires sequential deposition of multiple thin coatings, or parallel processing to deposit coatings on multiplexed structures; examples would include sensor arrays and multi-layer PLEDs. In such cases a solvent-free, vapor-phase coating technique could circumvent the difficulties associated with solvent compatibility and precise thickness control that are inherent in such liquid-phase deposition processes as spin-coating or dip-coating. We have previously demonstrated the possibility for ablation of intact polymers and other organic materials by infrared (IR) lasers tuned to resonate with a vibrational mode in the target [1]. In resonant infrared ablation, localized anharmonic vibrational modes are directly excited, generating the energy density and nuclear motion required for vaporization, by mechanisms that are still subjects of active investigation.

In this paper, we demonstrate preliminary results indicating successful deposition of polyimide precursor, without initiating the curing of this thermosetting polymer during the ablation process. In addition to illustrating the low-temperature property of resonant infrared pulsed laser deposition, this demonstration also exhibits a possible new route for deposition that is compatible with subsequent patterning of substrates and expanded uses of polyimide in the electronics industry.
2. Polyimides

Since their commercial introduction by DuPont in the 1960’s, polyimide films have been used as wire insulation, substrates for printed circuit boards, and solar panel cells. Powell and Lopez discussed the possibilities of PIs replacing polycarbonates as the standard for gas-filled windows (Hohlraums) and filters for x-ray astronomy [2]. Polyimides are synthesized by a two-step process (see Figure 1). First, a dianhydride and diamine are combined in a polar solvent to form the poly (amic acid) precursor (PAA); we used pyromellitic dianhydride (PMDA) and 4, 4’oxidianiline (ODA), dissolved in the solvent N-methyl pyrrolidinone (NMP). Our precursor solution of 15 wt% PAA in NMP was obtained from Sigma Aldrich. The choice of solvent affects the degree of cross linking and polymer chain length; NMP promotes longer chains prior to the cross linking step by increasing the melt flow. The second step requires a thermal cure to induce cyclodehydration; the PAA is heated to temperatures of 250 °C or greater to insure complete imidization. To prevent trapping of water vapour during the cure process, the film must be thin and uniform. Patterning of the PI is challenging because thermosetting polymers are not readily removed after curing, except possibly by UV laser ablation.

![Figure 1: Synthetic route to polyimide]([3]

3. Experimental Procedure

The ablation laser used in our experiments was an rf-linac driven free-electron laser (FEL) [4], wavelength tunable from 2 to 10 μm. The accelerator in the FEL is powered by an S-band klystron at 2.865 GHz that produces 4 μs macropulses at a repetition rate of 30 Hz. Within each macropulse, the small acceptance angle of the rf accelerator produces some 10^4 micropulses of approximately 1 ps duration. The optical bandwidth of the pulses is typically 1% of the center frequency (FWHM); the typical micropulse energy is several μJ, yielding a peak irradiance of order 10^9 W/cm². The total energy deposited is that of the macropulse, hence the fluence for the experiments reported here is that of the macropulse.

We first investigated laser ablation of commercially obtained amber-colored Kapton® tape approximately 63 μm thick with silicon adhesive on one side, at 5.9 μm wavelength corresponding to strong absorption in the C=O stretch mode. A film of the 15% PAA was formed by applying a thin layer to a glass slide and drying under moderate vacuum for 20 minutes.

For vacuum PLD experiments, the FEL beam was introduced into the vacuum chamber by way of a BaF₂ entrance window and focused onto the target by a 50 cm focal length BaF₂ lens. Using a pyroelectric joulemeter, we measured the transmission through the lens and entrance window to be approximately 0.8. The base pressure of our deposition chamber for the experiments in vacuum was 10⁻⁵ torr or less. The beam was rastered across the surface of the target at a frequency of 15 Hz while the target was rotated at 2 Hz to maintain a relatively even ablation across the surface of the frozen target.

Resonant infrared pulsed laser deposition (RIR-PLD) was used to transfer PAA under vacuum at ambient temperatures onto glass substrates. In RIR-PLD, it is typical for the polymer to remain in the elec-
tronic ground state during ablation, thus minimizing photochemical damage. Previous studies have shown that RIR-PLD is generally associated with temperature rises of only a few tens of degrees and with deposition rates substantially higher than those typical of UV PLD of inorganics. A solid target was made by freezing the PAA in liquid nitrogen for use in the chamber. An ablation wavelength of 3.45 μm was chosen to resonate with a strong absorption in the NMP, so that the NMP provided matrix-assisted ablation of intact PAA molecules. Material was deposited at fluences above 0.5 J/cm². The same wavelength was also used to transfer the precursor PAA in air. Additional RIR-PLD experiments were performed at the polymer resonant wavelength both under vacuum and in air.

The temporal evolution of the ablation plume was recorded by triggering a nitrogen laser-pumped Rhodamine 6G dye laser to illuminate the plume in shadowgraph mode, while a digital camera captured the image. The parameters of wavelength (6.67, 5.9, 4.8 and 3.45 μm), fluence (1-2 J/cm²) and polymer concentration (0, 1, 5, 10, 15 wt% PAA) were varied. Shock-wave velocities for different wavelengths (Figure 4) were obtained by measuring the shock front with a machinist ruler, with an error of order ±0.1 mm. Temporal jitter in the rise time of the FEL pulse causes only ns uncertainties in the time scale. A knife-edge measurement was used to obtain the spatial profile of the beam.

4. Discussion

After drying, the vacuum-deposited PAA film was transparent, contrasting with the amber coloured Kapton® tape. The supported Kapton® tape showed definable ablation above 3 J/cm², while the vacuum PAA film ablated at only 1.5 J/cm². Indicating greater ease of transferring the precursor compared to the cured PI. Transferring the liquid polymer precursor in air resulted in a pale yellow as-deposited material; it was readily removed by a solvent wipe with NMP. This simple experiment reveals that the PAA is transferred without an excessive temperature rise, allowing it to remain in the uncured state. After heating to 150 °C on a laboratory hotplate for 30 minutes, the deposited film could not be removed with an NMP wipe, although at that temperature it is likely that the film was not fully imidized. Moreover, as-deposited material did not change colour as would be expected if cross-linking and imidization had occurred; this also indicates little or no electronic excitation during ablation, since the characteristic amber colour of Kapton® and other PI films is due to electron transfer from diamine to dianhydride. Here, the colour change of the PAA from a transparent film at ambient temperatures to amber was seen only after prolonged heating.

Atmospheric and vacuum RIR-PLD showed a mixture of string and droplet morphologies when examined under the optical microscope. Atmospheric ablation at 3.45 μm (Figure 2) produced droplets, particularly with increasing fluence and a reduced target-to-substrate distance. Under vacuum at the same wavelength (Figure 3), the deposited material formed a network of strings with some small droplets interspersed. The droplets appear to result from expulsion of the solvent matrix, either by itself or with the solvent encapsulating some of the PAA. The droplet geometries dried into visually smoother films compared to the string morphologies. Of course, a smooth, uniform film is the ideal for most industrial applications. Further experiments will be required to determine which films possess the best overall qualities such as strength, uniformity, hardness, etc. PAA has also been transferred at 5.9 μm (not pictured), with similar material geometries. Holding all other parameters (target to substrate distance, fluence, and PAA concentration) constant, the 3.45 μm and the 5.9 μm wavelength do not produce the same film geometry, suggesting that there is a fundamental difference in the ablation mechanism between the polymer-resonant and the solvent-resonant wavelengths. More conclusive studies are needed to determine the precise effects of the resonant wavelength and of solvent-precursor interactions on film parameters.
FTIR spectra of PAA in NMP showed a strong absorption at 5.9 μm (carbonyl stretch), 3.45 μm (OH and CH stretches), 6.67 μm (aromatic ring mode), and no significant absorption at 4.8 μm (non-resonant). NMP also has a strong resonance at 3.45 μm (CH stretch); given the strong solvent interaction, 3.45 μm appeared to be an ideal solvent excitation wavelength. The infrared spectra of PAA in NMP vs. pure NMP show similar peak profiles with the PAA and pure NMP having approximately the same peak area for 3.45 μm, but with the PAA having a peak area double that of the NMP at 5.9 μm.

Figure 4 shows how the velocity shock front varied temporally with changing FEL wavelength. The polymer-resonant wavelengths (5.9 and 6.67 μm) generate a more rapidly expanding shockwave with peak velocities reaching 400 m/s. At the solvent resonance (3.45 μm) the shockwave expansion is delayed and only reaches a maximum velocity of approximately 300 m/s. The different wavelengths share a common velocity profile as shown below.

Ablation of the solvent alone (0% PAA) at 5.9 μm showed a vapor cloud initially, as time progresses an increasing amount of liquid is ejected. In contrast, the 15% PAA showed some initial liquid disturbance dying down to a vapor plume with a few liquid ejecta remaining. At times on the order of milliseconds, a diffuse “smoke” persisted from the polymer, which we hypothesize to arise from reactions with the air. Another notable difference is the greater dispersion of the polymer plume compared to the solvent plume (see Figure 5). The increased dispersion could be a result of the more rapid shockwave movement illustrated above. Changing the concentration and hence the viscosity of the liquid caused only minor differences at the same wavelength. Raising the fluence resulted in a more violent expulsion of material, but only minimally increased the propagation of the shockwave.
5. Conclusions

Although a number of thermoplastic polymers have been vaporized and deposited intact in previous experiments, the application of the RIR-PLD process to thermosetting polymers represents a qualitatively new and important demonstration of this process. Because these polymers set by cross-linking at temperatures around 250 °C, the successful deposition of uncured PAA illustrates the low-temperature character of RIR-PLD. Moreover, these preliminary experiments suggest that it should be possible to combine RIR-PLD deposition with post-deposition laser curing and patterning — a result potentially very desirable in many MEMS and microelectronics or microphotonics applications.

The excitation of the solvent NMP to facilitate the transfer of the polymer conceptually resembles matrix-assisted laser desorption-ionization (MALDI) mass spectrometry. However, the crucial difference is that the major product of the ablation is the neutral polymer species as opposed to ionic species. Similarities also exist between the process and ultra-violet matrix-assisted pulsed laser evaporation (UV-MAPLE) investigated by the Naval Research Laboratory group [5]. Once again the processes differ in several key respects: the energy for the PAA/NMP process is deposited into vibrational modes rather than the electronic modes activated by UV-MAPLE; the material from the PAA is ejected in a volumetric expansion as opposed to a surface ablation process, due to the substantially greater optical penetration depth of the IR radiation; and the PI precursor is transferred without curing, unlike UV ablation where the transferred material is often fragmented. The strong dependence of the shock velocity on wavelength, the relatively small effect of polymer concentration at the solvent-resonant wavelength, and the evident differences in plume expansion with and without polymer all suggest that the mechanism of vaporization in this case is quite different from MAPLE.

The current experiments also show a different ablation characteristic than the prior studies of IR laser ablation in Kapton® films. For example, the measurement of CO₂ laser ablation of Kapton® films showed shockwaves that had expansion velocities an order of magnitude larger than those observed here [6]. A higher degree of thermal damage to the material was also shown in the Kapton® film experiments. Working with the precursor solution to the PI gives a unique opportunity to minimize the thermal damage with RIR-PLD, while simultaneously maximizing the potential applications. While there are a number of unanswered questions in regards to the ablation mechanisms involved, the low-temperature nature of the RIR-PLD process and its potential for future application to other thermosetting polymers are evident.
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