Experimental studies and thermal modelling of 1064- and 532-nm Nd:YVO₄ micro-laser ablation of polyimide

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ABSTRACT Experiments and thermal modelling of polyimide ablation using the fundamental 1064-nm emission from a 20-kHz nanosecond diode-pumped solid-state Nd:YVO₄ micro-laser are described and compared with findings for the 532-nm doubled output. For exposures restricted to short pulse trains, it is found that micron-scale-size ablation features can be defined with this laser, even though polyimide films have weak absorption at 1064 nm and relatively weak absorption at 532 nm. There is evidence at both wavelengths of an incubation effect, driven by thermal modification of the polymer and, with long-term exposure at 1064 nm, Raman micro-spectroscopy reveals a progressive growth of predominantly amorphous carbon in the ablation site. Calculations of the temperature rise produced in the polymer by exposure to a high-repetition-rate pulse train are described that aid an understanding of the thermal aspects of the interaction at the two wavelengths.

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1 Introduction

Recent advances in diode-pumped solid-state (DPSS) micro-lasers have made available compact and efficient sources of nanosecond pulses [1, 2] of potential interest for use in laser ablation and micro-machining studies. Though restricted in terms of single-pulse energy, DPSS micro-lasers produce high-quality beams, making it possible to reach material ablation thresholds by focusing to small spot sizes using suitable optics. These small spot sizes, coupled with output pulse rates that may reach up to tens of kilohertz, place the ablation interaction in a regime that is different to that usually encountered, where large spot sizes and low pulse rates are the norm.

An early demonstration of the potential application of a DPSS micro-laser as an ablation source was provided by Gonzales and Baker [3], who investigated this for generating impulses for a satellite micro-thruster. In recent work we also reported that a Nd:YVO₄ micro-laser emitting at its fundamental and frequency-doubled wavelengths can successfully be used for machining fine features in various polymers, semiconductors and metal films [4]. In the present paper we describe experiments and thermal modelling of the ablation of polyimide using the fundamental 1064-nm emission from a nanosecond DPSS Nd:YVO₄ micro-laser and compare the findings with the results using the 532-nm doubled output. It is found that when exposure is restricted to a short pulse train, micron-scale-size ablation features can be defined with this laser, even though polyimide has weak absorption at 1064 nm and relatively weak absorption at 532 nm. At 1064 nm there is evidence that absorption increases through an incubation effect, but driven by thermal modification of the polymer rather than photomodification as seen with ultraviolet lasers [5]. Under long-term 1064-nm exposure Raman micro-spectroscopy reveals that there is a progressive growth of amorphous carbon in the ablation site, which modifies the interaction through the changes in optical properties this brings about. Calculations of the temperature rise produced in the polymer by exposure to a high-repetition-rate pulse train are described that aid an understanding of the thermal aspects of the interaction at the two wavelengths.

2 Experimental

Experiments were carried out on 125-µm-thick polyimide films (DuPont, Kapton HN) using a diode-pumped Nd:YVO₄ micro-laser (model AOT-YVO-3Q, AOT Ltd., Basildon, UK) emitting at either 1064 nm or 532 nm. The laser produced output pulses at a repetition frequency up to 20 kHz with a pulse length varying between 1.7 and 2.8 ns (full-width at half-maximum) depending on wavelength, repetition rate and drive current. A maximum average power of 530 mW was available at 1064 nm and 220 mW at 532 nm. A single-element plano-convex lens of focal length f = 38 mm was used to focus the 1064-nm beam and an f = 30 mm achromatic doublet for the 532-nm beam. The beam profile at the lens was measured using a profiling camera (OPHIR Beam Star). The films were mounted on a precision translator that allowed their precise positioning in the beam.

For exposure at 1064 nm the f = 38 mm lens was used at an aperture ratio of F = 3.2 with an input Gaussian beam radius of 8 mm (1/e irradiance). To account for spherical aberration in the lens, diffraction calculations were performed following the approach described in [6]. These showed that the irradiance distribution at best focus consisted of a well-defined central spot surrounded by weak diffraction rings. The central spot contained ~ 43% of the beam energy (Fig. 1).
and could be described approximately by a Gaussian distribution with a 1/e radius of 3.5 μm compared with 2.2 μm for ‘diffraction-limited’ performance. 1064-nm fluences specified in the present work are based on this calculated distribution. The achromatic doublet used at 532 nm gave a spot size of ~0.8 μm (1/e radius) on the assumption of diffraction-limited performance.

Transmission measurements on the Kapton film in the visible–near-infrared spectral region were made using a spectrophotometer (UV Unicam), and small-signal transmission and reflection during the course of film exposure to assess incubated absorption effects. Scanning electron and optical microscopy were used to characterise the morphology of the ablation sites. A Raman microscope (Labram, DILOR) with a 300-μW, 633-nm-wavelength probe laser and 1-μm spot size was used to investigate carbon formation in the ablation craters [7].

3 Results

Polyimide films absorb weakly at 1064 nm. An accurate determination of their absorption coefficient from the measured transmittance requires knowledge of the Fresnel reflection loss, which can be calculated if the refractive index is known. Spectrophotometer transmission measurements made on the 125 ± 2-μm-thick Kapton HN films produced no interference fringes because of insufficient coherence. However, for a 30-μm-thick Kapton 100 H film, well-resolved fringes were obtained and, from their spacing and the known film thickness, the refractive index at 1064 nm was deduced to be 1.587. Assuming this value to apply also to Kapton HN, a value for the 1064-nm absorption coefficient of α = 15 cm⁻¹ was calculated from the (incoherent) transmission of the film. For comparison a value of α = 17 cm⁻¹ was derived from reflection and transmission measurements made using the laser beam assuming, in this case, the interference to be coherent. Given uncertainties in the film thickness and the refractive index, a value of α = 16 ± 1.5 cm⁻¹ was thus taken for Kapton HN at 1064 nm. This absorption likely originates from inadvertent or deliberately added impurities [7] rather than being intrinsic to the polyimide itself. In contrast, the absorption coefficient is substantially larger at 532 nm because of the proximity to short-wavelength absorption bands in the polymer, and from the spectrophotometer transmission was found to be α = 120 cm⁻¹.

As previously reported [4], the ablation of Kapton HN using high pulse rate 1064-nm pulse trains is possible at modest fluence (~3–30 J cm⁻²) and appears to involve some degree of incubated absorption. This is seen as a delay in the visible inception of ablation (e.g. onset of a luminous ablation plume) and an initial increase in the etch rate as the number of pulses applied to the material is increased [4]. An example of the crater produced by exposure to 50 pulses at 1064-nm applied at 20 kHz in this fluence regime is shown in Fig. 2a. Here the peak on-axis pulse fluence based on the calculated irradiance distribution in the focal plane was 20.7 J cm⁻². The ablation crater has excellent definition, with a radius of ~3.7 μm compared with a predicted aberrated spot radius (1/e point) of 3.5 μm. There is evidence of a degree of swelling around the crater out to a diameter of about 10 μm, which is presumably associated with radial heat flow. Images from a Zygo white-light interferometer (NewView model 5032) of the same crater (radius ~3.7 μm) revealed a diameter of swelling ~22 μm. Similar swelling has been reported for polyimide exposed near the ablation threshold using a UV laser with small focal spots [8]. With reduced fluence somewhat smaller size spots could be obtained, an ex-
Fluence = 21 J cm$^{-2}$, 30 pulses were applied at 20 kHz. $\alpha \approx (1 - \exp(-0.0099 n^{-2})) \alpha_1 + \alpha_0$, $\alpha_1 = 114$ cm$^{-1}$, $\alpha_0 = 16$ cm$^{-1}$ and $d = 125 \mu m$

ample being seen in Fig. 2b where, with 50 pulses delivered at 20 kHz and a fluence of $\sim 12$ J cm$^{-2}$, an ablation crater with a radius just over 2.5 $\mu m$ is formed.

Monitoring of the transmitted laser pulses during exposure of the film confirmed that there is a growth in the effective absorption as the number of pulses increases. This is seen in Fig. 3, which shows the transmission for a 1064-nm pulse train delivered at 20 kHz and 21 J cm$^{-2}$. Beyond the eighth pulse the transmission falls to below 50% of that for the first pulse and then begins to level off after about 12 pulses, thereafter remaining approximately constant over long exposure intervals (e.g. 2000 pulses). It thus appears that after an initial growth in etch rate associated with ‘incubation’, this falls to a low value making complete drilling through of the film a very slow process.

Optical microscopy of the ablation sites showed that under prolonged exposure (e.g. 50–10 000 pulses at 20 kHz) a darkened zone with a sharply delineated circular boundary was formed (Fig. 4). The radius of this darkened zone (crater) is shown as a function of the exposure time in Fig. 5. With 100 pulses the crater radius is only $\sim 13 \mu m$, but this increases to $\sim 120 \mu m$ on exposure to 10 000 pulses. Stylus profiling confirmed that there was material removal/modification out to these large diameters, and showed that the crater depth reached $\sim 30–60 \mu m$ at its centre for 1000–4000 pulses. Interestingly, when samples that had been subjected to these large numbers of pulses were viewed using scanning electron microscopy (SEM), a highly textured micro-structure was observed to protrude from the surface (Fig. 6). This was more pronounced than seen under optical microscopy, suggesting that this disruption may arise, in part, through trapped gases being released from the thermally degraded polymer under the vacuum conditions of the SEM. These results indicate that there is an extensive heat-affected zone in the polymer under these quasi-continuous exposure conditions.

Raman spectra obtained at the centre of the ablation site (i.e. coincident with the 1064-nm laser spot) are shown in Fig. 7a for varying numbers of pulses, a base-line correction having been applied to remove the fluorescence contribution from the polyimide sample [7]. It can be seen
that two main peaks centred between 1323–1334 cm\(^{-1}\) and 1586–1597 cm\(^{-1}\) are present and that these initially grow in strength as the number of pulses increases. These are attributed to the presence of an amorphous form of carbon that has some degree of nano-crystallinity [9]. It was found that there was a level of carbonisation over the entire width of the ablation crater, although the strength of the signal fell off rapidly away from the centre (Fig. 7b).

Experiments were also carried out using the 532-nm harmonic wavelength where polyimide exhibits a significantly higher absorption coefficient and a correspondingly lower multiple-pulse ablation threshold (\(\sim 0.2\) J cm\(^{-2}\)) than at 1064 nm [4]. By restricting exposure to short pulse trains (e.g. \(\sim 10\) pulses at 20 kHz) it was possible to produce small-diameter ablation features of excellent quality, as illustrated by the example in Fig. 8. Here the spot has a radius of 1.1 \(\mu\)m and is close to that expected for diffraction-limited performance of the achromatic doublet [4]. At this wavelength the transmission fell abruptly after the first pulse and then declined more slowly over 30 or so pulses to a low steady value. This fall could be associated with an increase in near-surface absorption or with scattering/refraction at the ablation site or a combination of these effects. As a large-area photodiode located close to the rear surface of the film was used, it is likely that most of the transmitted radiation was collected and the change is therefore connected with absorption rather than scattering/refraction. Prolonged exposure again
produced a darkened zone around the laser-interaction site that increased in diameter with time, indicative of carbonisation occurring in the heat-affected zone.

Qualitative resistance measurements on craters and micro-channels [4] formed using the 1064-nm and 532-nm lasers were made using point probes and a Keithley Instruments, model 177, digital multimeter. A dramatic rise in conductivity was found in the craters, presumably associated with the formation of carbon networks analogous to reports for low fluence excimer laser [10] and cw UV laser irradiated polyimide [11].

4 Temperature-rise modelling and discussion

To model the temperature rise produced in the polyimide film by a train of pulses we make the simplifying assumption that, for exposure to a modest number of pulses, only radial heat flow contributes to cooling the heated region. This is reasonable if the characteristic absorption depth greatly exceeds the radial dimension of the focal spot, i.e. \( \delta = (\alpha a)^{-1} \gg 1 \), where \( \alpha \) is the absorption coefficient and \( a \) is the Gaussian spot radius (1/e fluence). Taking \( a \leq 5 \mu \text{m} \) we obtain \( \delta \geq 16.6 \) at 532 nm where \( \alpha = 120 \text{ cm}^{-1} \), and \( \delta \geq 125 \) at 1064 nm where \( \alpha = 16 \text{ cm}^{-1} \), so that this assumption appears justifiable. The temperature-rise distribution, \( T(r, t) \), following the initial, essentially instantaneous, increase produced by the nanosecond laser pulse is then found from [12]:

\[
T(r, t) = T_0 \int_0^\infty \exp \left[-z^2/(2\alpha^2)\right] \left[-(z^2 + r^2)/4\kappa t\right] I_0(rz/2\kappa t) \, dz = (2\kappa t)^{-1/2} I_0(r/s),
\]

where \( I_0 \) is the zero-order modified Bessel function and \( \kappa \) is the thermal diffusivity of the polymer. Here the initial temperature rise is taken to have a Gaussian distribution with a value at \( r = 0 \) given by \( T_0 = (1 - R)\alpha F_0/C \), where \( C \) is the volume specific heat of the polymer and \( F_0 \) is the peak laser fluence. Equation (1) can be evaluated in terms of a standard integral, giving

\[
T(r, t) = T_0 \left[ \exp \left(-r^2/[4\kappa t + \alpha^2]\right) \right] / (4\kappa t/\alpha^2 + 1). \tag{2}
\]

The temperature rise produced by a train of \( n \) pulses is then found by summation:

\[
T_n(r, t) = \sum_{n=1}^{n-1} T(r, t - n/v),
\]

where \( v \) is the pulse-repetition frequency (prf).

To simplify the temperature-rise modelling, the widely dispersed fraction of energy lying outside of the central spot of the aberrated 1064-nm beam (Fig. 1) was neglected, on the assumption that this would have only minor influence on the temperature distribution. The data in Table 1 were used for polyimide, neglecting any temperature dependence of these thermo-optical parameters.

Figure 9a shows the surface-temperature rise versus time at \( r = 0 \) and \( r = 1.5a \) calculated using (2) for a single pulse at 1064 nm with a focal spot radius of \( a = 3.5 \mu \text{m} \) and a fluence \( F_0 = 20.71 \text{ cm}^{-2} \). At \( r = 0 \) the time constant for cooling to 50% of the peak temperature rise is 30 \( \mu \text{s} \). A consequence of this relatively slow cooling is that there is a significant cumulative heating when a train of 10 pulses is applied at 20 kHz (Fig. 9b), with the peak temperature rise at \( r = 0 \) reaching 462 K by the 10th pulse. Comparing the radial temperature profile produced by a single pulse with that just after the 10th pulse, Fig. 9c, shows that there is considerable broadening of the distribution by radial heat flow, i.e. a radial width \( \sim 5.8 \mu \text{m} \) at the 1/e point. The effect of increasing the pulse number to 50 at 20 kHz, as used to obtain the result in Fig. 2, is seen to raise the maximum temperature increase to 651 K (Fig. 10). The corresponding radial temperature distribution has then reached a near-steady state, with a 1/e width of \( r = 9.3 \mu \text{m} \) just after the 50th pulse.

The temperature rise predicted by this modelling using the intrinsic absorption coefficient of polyimide is too low, even out to 50 or more pulses, to explain the onset of ablation. Based on Küber et al.’s [13] deductions from long-wavelength UV laser experiments, thermally initiated ablation of polyimide is expected to commence only if the surface-temperature rise exceeds \( \sim 850 \text{°C} \). However, this picture is altered when account is taken of the apparent increase in absorption that occurs with an increasing number of pulses. The phenomenon of ‘incubated’ absorption plays a significant role in the ablation of weakly absorbing polymers and at UV wavelengths is associated with a photo-induced change in chemical structure of the polymer that increases its effective absorption coefficient [5]. For polyimide, incubation effects are likely associated with carbon formed through photochemical degradation steps [14], thermally induced degradation [11, 15] or a combination of these mechanisms [16] depending on the laser wavelength. In any case this behaviour appears to be relatively independent of the pulse length or intrinsic absorptivity involved.

To quantify the effect ‘incubated’ absorption has on the temperature rise, we assume that the reduction in laser transmission is the result of a spatially uniform increase in the absorption coefficient. On this basis an empirical fit to the transmission results in Fig. 3 gives an absorption coefficient that increases with the number of pulses \( n \) according to \( \alpha \approx (1 - \exp(-0.00999n^2))\alpha_0 + \alpha_1 \), where \( \alpha_0 = 16 \text{ cm}^{-1} \) and \( \alpha_1 = 114 \text{ cm}^{-1} \). \( \alpha \) is then initially 16 cm\(^{-1} \), rising to a steady value of \( \sim 130 \text{ cm}^{-1} \) beyond about 15 pulses. Including this pulse-to-pulse increase in \( \alpha \) in the temperature-rise modelling has a major influence, as can be seen from Fig. 10. By the seventh pulse the temperature rise reaches 1010 K, which is expected to be sufficient to initiate ablation on the time scale available [13]. It should be noted that strictly this simple heating model will break down once ablation sets in, as no account is taken of energy loss to decomposition or to that carried away from the surface by the ab-

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Thermal diffusivity ( \kappa )</td>
<td>( 1 \times 10^{-3} \text{ cm}^2 \text{s}^{-1} )</td>
</tr>
<tr>
<td>Volume specific heat ( C )</td>
<td>1.55 J cm(^{-3}) K(^{-1})</td>
</tr>
<tr>
<td>Low signal absorption coefficient ( \alpha )</td>
<td>( 16 \text{ cm}^{-1} ) at 1064 nm</td>
</tr>
<tr>
<td>Reflection coefficient ( R )</td>
<td>0.05</td>
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<tr>
<td></td>
<td>( 120 \text{ cm}^{-1} ) at 532 nm</td>
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TABLE 1 Thermo-optic parameters for polyimide
Temperature rise calculated for 1064-nm laser exposure of polyimide with $a = 3.5 \mu m$ (1/e fluence) focal spot radius. Peak fluence = 20.7 J/cm$^2$.

Temperature rise as a function of time for single-pulse exposure at locations of $r = 0$ (---), $r = a$ (– – –) and $r = 1.5a$ (−−−).

Temperature rise at centre of focal spot for a train of 10 pulses applied at 20 kHz, radial temperature distribution produced by a 20-kHz pulse train at the 10th pulse (curve a) and 20µs after the 10th pulse (curve b). Curve c shows initial temperature profile for single pulse.

FIGURE 10 a Temperature–time profile at centre of laser spot ($r = 0$) for 50 pulses at 1064 nm applied at 20 kHz. Lower trace: constant absorption coefficient $\alpha_0 = 16 \text{ cm}^{-1}$. Upper trace: absorption coefficient varying with number of pulses $n$ as $\alpha = [(1 - \exp(-0.0099n^2))\alpha_1 + \alpha_0]$ with $\alpha_0 = 16 \text{ cm}^{-1}$ and $\alpha_1 = 114 \text{ cm}^{-1}$. b Radial temperature rise profile at the 50th pulse for exposure as above. − With incubated absorption, −−− without incubated absorption, −−−− initial distribution produced by single-pulse exposure. Fluence = 20.7 J/cm$^2$, $a = 3.5 \mu m$

The origin of the 1064-nm incubated absorption is tentatively attributed to thermal reactions that initiate carbonisation of the polymer or act to amplify any pre-existing absorbing particles that may be present. Butenin and Kogan [17] have analysed the role of carbon inclusions with regard to damage mechanisms in transparent polymers and show that even nanoscale particles can act as effective absorption centres. These particles are heated to high temperatures by the laser pulse, enabling them to grow in size by initiating decomposition and carbonisation in their immediate vicinity. This effectively raises their cross section for subsequent pulses, leading to a further increase in temperature rise on so on [17] until microscopic damage sets in. These carbon particles may be present as microscopic impurities in the film [17] or, as seems more likely in the present case, the product of heating and degradation induced by the first few laser pulses in the train. Weight-loss degradation of Kapton HN is known to commence above about 450 °C in air [18], a value that the modelling shows should be reached in the early stage of the interaction. In either case, such absorbing centres can grow in size resulting in an increase in the (volume-averaged) polymer

...
temperature rise, until this becomes high enough to promote rapid decomposition and ablation. This increase in effective absorption is confirmed by the laser transmission results in Fig. 3.

The large zone of ‘ablation’ produced at long exposure times (Figs. 4 and 5) cannot be understood in terms of the simple radial heat flow model outlined above. The quasi-steady temperature profile produced in the polymer under these conditions has a radius that reaches only $\sim 10 \, \mu m$, whereas the darkened zone (‘crater’) measured from optical micrographs is much larger, e.g. $\sim 120 \, \mu m$ at $t = 0.5 \, s$ (10000 pulses). This is attributed to a change from relatively weak distributed absorption in the pristine polymer to a strongly localised absorption that accompanies carbonisation in the laser spot region. The growth of this carbon fraction is clearly confirmed by the Raman spectra. To treat this case we assume that the absorption is sufficiently high so that the laser becomes a surface source and calculate the resulting temperature distribution by modelling this as a disc of point heat sources [12]. Then, assuming that the crater boundary is defined by the point where the temperature falls below some value, $T_D$, needed to induce decomposition, the predicted ‘decomposition’ radius could be plotted versus time. The results of this surface-source calculation are shown in Fig. 5, where the datum point at $t = 0.5 \, s$ has been normalised to the experimentally determined radius (corresponding $T_A = 2300 \, K$). As is evident, there is good agreement between the predicted and experimental radii at times down to $\sim 0.025 \, s$. The divergence at shorter times is attributed to the shift from surface to distributed absorption as the degree of carbonisation decreases. In addition, for shorter heating times, it is expected that the boundary will correlate with a larger temperature rise because there is less time available for decomposition.

It is of interest to compare the 1064-nm results with those predicted for the 532-nm laser where the absorption is higher and a smaller focal spot size is attainable. Figure 11 shows the calculated temperature rise for a spot size of $a = 1 \, \mu m$ and a fluence $F_0 = 31.8 \, J \, cm^{-2}$. The cooling is now more rapid because of the reduced spot size, with the single-pulse temperature falling to 50% of its peak value in just 2.4 $\mu s$ (Fig. 11a). The cumulative heating effect from a pulse train is significantly reduced because of this rapid cooling, as is clearly evident from Fig. 11b, which shows 10 pulses applied at 20 kHz. The corresponding radial temperature distribution at the 10th pulse and 2 $\mu s$ after this is shown in Fig. 11c, together with the initial ‘single-pulse’ distribution. There is a notable difference with Fig. 9c, as the ‘single-pulse’ profile is essentially retained over the entire pulse train, with only a low-amplitude temperature ‘pedestal’ being produced through radial heat diffusion. Thus, although the absorption is still relatively weak at this wavelength, the small spot size and the short heating–cooling cycle give a result that is qualitatively similar to that in a stronger absorber where axial temperature gradient mainly determines the cooling rate. Under these conditions it is anticipated that thermal ablation should remain localised, with lateral dimensions of the same order as the focal spot size. This is confirmed by the result in Fig. 8, which shows that it is possible to define a $\sim 1-\mu m$-radius ablation crater in polyimide with the 532-nm beam [4]. Clearly, more detailed modelling would need to take account of an increase in effective absorption when exposure is over an extended duration. Under these conditions the craters appear to evolve in a similar way to those at 1064 nm, suggesting that progressive carbonisation occurs and again a change from a distributed to a surface absorption.

\textbf{FIGURE 11} Temperature rise calculated for 532-nm laser exposure of polyimide with $a = 1 \, \mu m$ ($1/e$ fluence) focal spot radius. Peak fluence = 31.8 J cm$^{-2}$. \textit{a} Temperature rise as a function of time for single pulse at locations — $r = 0$, $\ldots$, $r = a$ and $- - - - - r = 1.5a$. \textit{b} Temperature rise versus time for a train of 10 532-nm pulses at 20 kHz. \textit{c} Radial temperature rise distribution showing profile just after 10th pulse (\textit{curve A}), 2 $\mu s$ after 10th pulse (\textit{curve B}) and the initial value for the first pulse (\textit{curve C}).
As a final observation, we note that carbonisation appears to play two competing roles in the ablation of polyimide (at least at 1064 nm). At low pulse numbers it produces the necessary increase in absorption and hence temperature rise to initiate ablation. However, with prolonged exposure a more extensively carbonised layer is formed that becomes increasingly resistant to ablation, producing a fall or even a halt in the etch rate. This makes it difficult or impossible to drill completely through a thick film. Ball et al. [19] have made a detailed study and analysis of this for polyimide irradiated using a pulsed 248-nm laser, concluding that both surface roughening and compositional change are implicated in the etch-rate reduction. It seems likely that similar processes are operative here, although the initial route to carbon formation is different.

5 Conclusions

These studies show that a nanosecond-pulse Nd:YVO₄ micro-laser operating at 1064 and 532 nm can be used to produce micron-scale ablation features in polyimide. At the fundamental wavelength this polymer has weak absorption and under multiple-pulse exposure thermal ablation appears to be initiated by thermal degradation that leads to the formation of absorbing amorphous carbon. This carbonisation is confirmed by Raman microscopy. For long trains of pulses thermal modelling incorporating incubation indicates that the radial heating will expand the diameter over which there is degradation to a much larger value than the focal spot. To minimise this it is necessary to confine high pulse rate exposure to short dwell times (e.g. 10–50 pulses at 20 kHz). It is then possible to produce features of ~10-μm diameter, although with processing restricted to relatively modest depth. Carbonisation has the beneficial effect of lowering the ablation threshold for early pulses in a train but over extended exposure times may reach such a level that surface layers become increasingly resistant to ablation, restricting the ability to efficiently etch deep features; it can also compromise the insulating properties of the material.

At 532 nm where smaller spot sizes can be achieved, rapid radial cooling acts to reduce the overall duration of the heating–cooling cycle. Modelling shows that this restricts the radius over which there is a substantial temperature increase, confining ablation to the same characteristic size as the focal spot even with extended duration pulse trains. Processing with these small spot sizes is thus advantageous and enables micron-scale features to be defined even though the polymer has weak intrinsic absorption.

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