Laser removal of paraffin wax from glass surfaces

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Waxes and thermopolymers are commonly used to mount optical and photonic materials prior to polishing and singularization. After demounting, residual wax/thermopolymer can adhere to the component surface, frequently in the form of particles. Dry, ultraviolet-pulsed laser cleaning has been demonstrated to effectively remove paraffin wax particles, prepared on a glass surface using a wax aerosol technique. This method produces dome-shaped particles. Experimental evidence suggests the dome-shaped particles are vaporized by the absorption of the energy from the laser pulse. A theoretical model based on vaporization has been developed and this leads to predictions of the critical fluence for single laser pulse removal of dome-shaped particles which is in good agreement with that experimentally measured (220 mJ/cm²). The model also gives insight into the geometries and relative thermal properties of the “particles” and surface, which are important in determining whether removal by vaporization is a viable process. © 2002 American Institute of Physics. [DOI: 10.1063/1.1509097]

I. INTRODUCTION

Laser cleaning of particles from surfaces is a technique that has been tested in a large variety of particle/surface material systems, particularly for industrial applications in semiconductor and optics/photonics contexts. Pulsed lasers with a range of wavelengths have been used. The processes by which particle removal occurs involve explosive vaporization or boiling of a liquid film in wet laser cleaning, rapid expansion of the surface and/or the particle in dry laser cleaning, and possibly other nonlinear and surface acoustic wave mechanisms. Additionally, the laser cleaning technique has been applied to removing films and hydrocarbon contaminants from surfaces. Even continuous wave lasers have been used to successfully remove contamination, such as fingerprints, from surfaces. The current belief in the laser cleaning research field is that “any laser can be used to remove hydrocarbons.” Motivated by our own experimental observations that this is not always the case, we report a systematic study of removal of paraffin wax from glass surfaces.

Waxes and thermopolymers are commonly used to mount optical and photonic materials for polishing and singularization. After demounting, residual wax/thermopolymer can adhere to the component surface, frequently in the form of particles. Standard wet chemical cleaning and plasma-cleaning techniques are commonly used to remove the residue but this involves taking the components out of the production line to a cleaning tool. A noncontact method of cleaning that can be incorporated into the production line is regarded as highly desirable. Dry/damp, ultraviolet (UV)-pulsed laser cleaning has been demonstrated to effectively remove particles (example alumina) from glass. In the research reported here, a KrF excimer laser at 248 nm has been used to evaluate dry laser cleaning of samples prepared by spraying an aerosol of melted paraffin wax on glass microscope slides. This resulted in dome-shaped paraffin “particles” with diameters in the range of 1–20 μm. Effective laser cleaning was achieved at modest fluences (fluences up to 220 mJ/cm² have been studied). There was no evidence of optical damage occurring in parallel with the laser cleaning. These results contrast with experimental results obtained using photonic components, sourced from photonic device production lines, where it was found that some of the residue of the optical mountant still on components after wet chemical cleaning was in the form of particles that cannot be laser removed before the threshold for optical damage is reached.

A thermal model of the laser removal process has been developed for quantitative predictions of the critical fluence of a single laser pulse required to remove a dome-shaped particle of paraffin wax by vaporization. The results from the theory are compared with the experimental results and good agreement is obtained. The model also gives insight into material systems and geometries where effective removal by vaporization is likely to be achieved, and those where effective removal is unlikely.

II. EXPERIMENT-SAMPLE PREPARATION

Samples were prepared using paraffin wax as the “particle” material and glass microscope slides as the substrate. The wax used in this analysis was paraffin with 5% cerasin. It has a congealing point of ~60 °C. Paraffin wax is present in crude oil and is a by-product of crude oil refinery processes. Waxes, derived originally from plant matter, are mixtures of many constituents, with important ones being esters of fatty acids with alcohol. Paraffin wax has straight chain hydrocarbon constituents and can have a melting point in the range of 49 to 71 °C, depending on its more detailed composition.

The thermal reference data for paraffin wax is
TABLE I. Thermal properties for paraffin wax and other substances.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cp (J/kgK)</th>
<th>Cv (J/kgK)</th>
<th>Lf (J/kg)</th>
<th>Lv (J/kg)</th>
<th>Density (kg/m³)</th>
<th>Melting temperature (°C)</th>
<th>Thermal conductivity (W/mK)</th>
<th>Boiling temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin wax</td>
<td>2900b</td>
<td>1.46 × 10b</td>
<td>800</td>
<td></td>
<td>0.231 W/mK</td>
<td>200 (Flashpoint)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canauba wax</td>
<td>3300</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Beeswax</td>
<td>1.74 × 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Alkanes (Paraffin oils)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffinic blend</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oil d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water e</td>
<td>2089</td>
<td>4169</td>
<td>3.33 × 10</td>
<td>2.255 × 10</td>
<td>1000 (0 °C, 1 atm)</td>
<td>0</td>
<td>1.5 × 10⁻⁴ (ice)</td>
<td>100</td>
</tr>
<tr>
<td>Ethanol e</td>
<td>1.04 × 10</td>
<td>8.54 × 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.6 × 10⁻⁶ (water, 20 °C)</td>
<td>78</td>
</tr>
<tr>
<td>Silicon f</td>
<td>700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2590</td>
</tr>
<tr>
<td>SiO₂ f</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass b</td>
<td>772</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.1 × 10⁻⁷</td>
<td>2590</td>
</tr>
<tr>
<td>Alumina b</td>
<td>754</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.8 × 10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

References:
- a Reference 8–11.
- b Reference 9.
- c Reference 10.
- d Reference 12.
- e Reference 11.
- f Reference 14.
- g Reference 15.
- h Reference 13.
- i Reference 16.
- j Reference 11.

Incomplete but some thermal property reference data for waxes, and other materials with which paraffin wax can be compared, are given in Table I.

The key thermal reference data values that are not available for paraffin wax, and which are needed to calculate the energy required to vaporize a certain mass, are the latent heat of vaporization and the boiling point. Paraffin wax is expected to be like water and organics (e.g., ethanol), which have a latent heat of vaporization of the order of 6.5–8.5 times the latent heat of fusion for the material (Table I). Such materials contrast strongly with, for example, metals, where the latent heat of vaporization is some 20–25 times that for fusion. Thus, it is estimated that the latent heat of vaporization for paraffin wax is 1.1 × 10⁶ J kg⁻¹, with an uncertainty of the order of 2 × 10⁵ J kg⁻¹. To estimate the boiling point of paraffin wax, we note that there is no evidence of combustion of the paraffin wax caused by laser irradiation in the experiments carried out, and hence we propose that the boiling point is below the flashpoint (Table I), and it is set it to be 200 °C. The data in Table I for paraffinic mineral oil has the boiling point more than 150°C above the flashpoint for that liquid so it is possible the boiling point for paraffin wax is higher. The energy needed to provide the latent heat of vaporization to a mass of paraffin is by far the largest component of the total energy. Thus, any error in the boiling point temperature is not critical to energy calculations. Similarly, the energy required to heat the solid and liquid paraffin between phase change temperatures is small compared to that associated with vaporization and thus the specific heat value for solid paraffin wax is assumed to apply to the liquid form also.

The dome-shaped paraffin wax particles were prepared by spraying liquid paraffin onto the glass microscope slide using a simple atomizer. The liquid paraffin (after heating beyond the melting point) was drawn up a thin tube by the venturi effect and converted to a fine spray by a burst of compressed air. The slide was held vertically approximately 1 m from the atomizer nozzle. This method produced a layer of evenly distributed particles of spherical cap (dome) shape upon the substrate surface. The particles ranged in size from approximately 1 to 20 μm in diameter. A close-up of the dome-shaped paraffin particles on the surface is shown in Fig. 1.

The substrates were prepared by ultrasonically cleaning glass microscope slides in a 10% isopropyl alcohol solution for 15 min. The slides were rinsed with excess isopropyl alcohol and dried in air. Lens tissue solvent wipes were sometimes used to dry the samples if drying in air left any visible residue on the glass surface.

III. EXPERIMENT-LASER CLEANING

The experimental setup used for laser cleaning the paraffin on glass slide samples is shown in Fig. 2. The laser used...
was a PulseMaster PM-848 KrF excimer laser, manufactured by GSI Lumonics (wavelength 248 nm, pulse length 25 ns, pulse energy up to 80 mJ, beam size $\sim 2.5 \text{ cm} \times 1 \text{ cm}$). A spherical lens was used to focus the beam to a smaller size so that several regions could be irradiated with different fluences on the same sample. A beam size of approximately $8 \text{ mm} \times 3 \text{ mm}$ was used. A beam attenuator (OPTEC AT-4030) was placed in the beam path before the spherical lens to vary the laser-pulse energy (and hence fluence, calculated as the measured pulse energy divided by the beam area at $\sim 20\%$ of peak value for a flat-topped beam with slightly sloping sides) without altering the laser operating conditions or the focussing optic. The attenuator was used to vary the energy of the irradiating pulse between zero and maximum energy.

Computer controlled motorized stages (Physik Instrumente C-842 Version 2.20) were used to move the sample in and out of the beam path for off-line monitoring and to position the target area in the desired location for irradiation.

The sample was monitored with an optical microscope (Olympus CHD) at a magnification of 100×. Images were viewed using a charge-coupled device camera (Pulnix TM-6CN) attached to the microscope and a Sanyo high-resolution monitor. Images before and after irradiation were captured via a frame grabber (Data Translation DT-55). The resulting images were processed and recorded with Global Lab image processing software. The total area irradiated was monitored by joining several images within the irradiated area end to end. An area of $530 \mu\text{m} \times 350 \mu\text{m}$ was recorded in each image at magnification of 100×. Detailed image processing and particle analysis was later performed with the Media Cybernetics’ Image Pro Plus software package.

IV. RESULTS-LASER CLEANING

A composite of 20 images, each of an area $530 \mu\text{m} \times 350 \mu\text{m}$, both before and after cleaning with a single laser pulse of fluence $218 \text{ mJ/cm}^2$, is shown in Fig. 3. The images are taken from the middle section of the irradiated area and cover the full length of the beam in the horizontal direction. To make sure that the entire beam width is observed, the first and last images are positioned so that the beam edges fall approximately in the center of these images. The regions at the ends of the long axis of the beam show little evidence of cleaning as shown in Fig. 4 where the number of particles in each individual image before and after laser cleaning ($218 \text{ mJ/cm}^2$) are shown. The profile of particle removal follows the intensity profile of the laser beam quite closely. The total number of particles, categorized by particle radius, before and after laser cleaning, are shown in Fig. 5, for all twenty images. As laser cleaning is efficient in the region of the beam where the intensity is constant the analysis is limited to images 7–14 in the middle section of the beam in Fig. 6(a). The results for three lower pulse fluences, for images

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**Fig. 1.** High-magnification ($\times 2500$) picture depicting the domelike shape of contaminant particles.

**Fig. 2.** Schematic of the experimental layout used for laser cleaning of paraffin from glass slide samples.

**Fig. 3.** Images of the paraffin particles on the glass slide before and after irradiation with a KrF excimer laser pulse of fluence $218 \text{ mJ/cm}^2$.
FIG. 4. Spatial distribution of particles before and after irradiation with a 218 mJ/cm² laser pulse.

7–14 are shown in Figs. 6(b)–6(d). The fluence was reduced using an attenuator and hence the beam profile was the same at all fluences. At the lower fluences, particles reduced in size were often observed after irradiation, rather than being completely removed, providing evidence of vaporization as the major factor in particle removal. There were a small number of observations of larger particles increasing in size which could be explained by changes in surface tension when the paraffin wax melted leading to spreading and thinning of the dome.

The laser cleaning efficiency is defined as

\[ 100 \frac{(N_B - N_A)}{N_B} \% , \]

where \( N_B \) and \( N_A \) are the number of particles before and after laser cleaning, respectively. The cleaning efficiency results are plotted for the total number of particles (in images 7–14) as a function of fluence in Fig. 7. From the fit to these results, it is seen that paraffin wax removal is initiated at a fluence of a few mJ/cm². Thus, multiple pulse treatments at these low fluences would be able to remove paraffin. The cleaning efficiency results as a function of particle size are plotted for four fluences in Fig. 8. It should be noted that for particles of size 1 \( \mu m \) and those greater than 12 \( \mu m \), there are fewer than 10 particles present in the samples before laser cleaning so the statistical confidence level in the cleaning efficiency is not as high for these particle sizes.

V. THEORY

The paraffin-wax particles on the glass slide prepared by using an atomizer are dome shaped. When a low fluence pulse is used, the larger dome-shaped particles become smaller rather than being completely removed. This experimental result suggests that a model based on vaporization of the paraffin wax particles should be tested. For the particle to be removed by vaporization, the energy absorbed in the particle must equal or exceed the energy \( E_v \) required to vaporize the particle. \( E_v \) is composed of the energy required to heat the mass of the particle from room temperature to the vaporization temperature for the wax, plus the energy required to effect the phase change from solid to liquid and from liquid to vapor, as shown in Eq. (1). The mass of the particle is \( m \), \( C_s \), and \( C_l \) are the specific heat capacities of the solid and liquid paraffin which are assumed equal, and \( L_f \) and \( L_v \) are the latent heats of fusion and vaporization, respectively. \( \Delta T_1 \) and \( \Delta T_2 \) are the temperature differences between room temperature and the melting temperature, and the melting temperature and the boiling point temperature, respectively.

\[ E_v(m) = m[C_s\Delta T_1 + C_l\Delta T_2 + L_f + L_v] \]
\[ = m[C_s(\Delta T_1 + \Delta T_2) + L_f + L_v] . \quad (1) \]

The mass, \( m \) of the dome-shaped paraffin wax particle is calculated by first finding the volume and multiplying this by the density of paraffin wax. It is assumed the dome-shaped particle is the cap of a sphere of radius \( R_s \) as shown in Fig. 9. The radius of the particle is \( R_p \), and this is related to the radius of the sphere by

\[ R_s = [(R_p^2 + h^2)/2h] . \quad (2) \]

The volume of the dome is given by

\[ V_p = \frac{\pi}{3} h^2(3R_s - h) . \quad (3) \]

A single laser pulse of fluence \( F_l \) delivers an energy of up to \( F_l \pi R_p^2 \) to the dome-shaped particle, for normal incidence and total absorption. In this case, the critical fluence \( F_{lc} \), required to remove the dome-shaped particle by vaporization is given by

\[ F_{lc} = E_v(m)/\pi R_p^2 = E_v(R_p, h)/\pi R_p^2 . \quad (4) \]

The assumption that all the energy is absorbed by the particle appears to be a reasonable one as will be discussed later.
However, $F_{lc}$ can be scaled for fractional absorption and non-normal incidence if this is deemed appropriate or necessary.

In calculating $F_{lc}$, two different hypotheses, relating $R_p$ and $h$, have been tested. These are illustrated in Fig. 10. First, it is assumed $h$ is held constant [Fig. 10(a)] and in this case, $R_s$ is a function of both $h$ and $R_p$. In this first case, the critical fluence is found to be independent of the value of $R_p$ when $h$ is much smaller than the particle radius. Second, it is assumed the height of the dome above the surface is a constant fraction of $R_p$ [Fig. 10(b)]

$$h(R_p) = R_p/a,$$

where $a$ is a constant which is varied between values of 1 and 50 in the calculations that have been carried out. In this

FIG. 6. Particle size distribution before and after irradiation for images 7–14 using a laser pulse with fluence (a) 218, (b) 103, (c) 51, and (d) 31 mJ/cm².

FIG. 7. Cleaning efficiency of paraffin wax domes from glass as a function of laser-pulse fluence.
second case, \( R_s \) is a function of \( R_p \) only. In all calculations, \( h \), the height of the dome must be less than or equal to \( R_p \) for Eqs. (2)–(4) to be valid.

VI. THEORY-RESULTS AND DISCUSSION

The results of calculations of the critical fluence (single laser pulse) for removal of a dome-shaped particle of paraffin wax by vaporization are shown in Figs. 11 and 12. The thermal properties for paraffin wax listed in Table 1 and estimated in Sec. II have been used.

The results of assuming a constant value of \( h \), which is then varied, are shown in Fig. 11 for three values of the particle radius (solid lines). The dashed lines show the bounding values the critical fluence could take allowing the latent heat of vaporization for paraffin wax to be in the range \((1.0–1.2) \times 10^6 \text{ J kg}^{-1}\). When the dome height is small compared to the particle radius or the particle is small, the critical fluence is independent of the particle size as shown in the inset (results for \( h \) up to 1 \( \mu \)m on an expanded scale). The critical fluence for a given dome height is larger for smaller radius particles than for larger radius particles, indicating that for this model, smaller particles are harder to remove, but marginally so. A model of columnar particles would be seen to make a significant difference in this regard. The critical fluence would then grow linearly with the height of the column and, “particles” with a small cross-sectional area and large height will be very difficult if not impossible to remove by vaporization.

The results from using \( h(R_p) \) in the form given in Eq. 5 are shown in Fig. 12. It is clear that as the dome height becomes a larger fraction of the particle radius, the critical fluence increases rapidly. The dependence is supralinear when the critical fluence is plotted against \( 1/a \) rather than \( a \). The critical fluence scales linearly with the particle radius for a given value of \( a \) as shown by the inset in Fig. 12. These results show that “flatter” domes are more easily removed, as expected.

For successful removal of the paraffin wax contaminant while the substrate remains unaffected, the thermal properties of the substrate must also be considered. The much higher melting point for glasses of \( \approx 1000–1200 ^\circ\text{C} \) (with a change to a different solid phase occurring at \( \approx 800 ^\circ\text{C} \)) means that no phase change in the bulk or the surface of the glass needs to be considered at the fluences that are found to remove the paraffin wax with its low-melting point. In considering the process by which the paraffin wax domes are vaporized, and the reduction in size that occurs when complete removal is not achieved, the low-thermal conductivity of the material may also be important. Dynamically, it may
be the case that the paraffin wax is vaporized as a propagating thin film. The low-thermal conductivity then facilitates rapid heating at the exterior surface of the dome and the pulse length of the laser pulse needs to be sufficiently long for the complete removal of the whole dome. Significantly, shorter pulses might not be as effective in this process. It remains an interesting question for future work to consider the time-resolved removal of the paraffin wax.

VII. COMPARISON OF THEORY AND EXPERIMENT

The two models of dome-shaped, paraffin wax particles predict quantitative values for the critical fluence for removal by vaporization which can be compared with the experimentally determined threshold fluence for removal by vaporization, effected by absorption of a single UV laser pulse. From the experimental results [Fig. 6(a)], it is seen that a laser-pulse fluence of 218 mJ/cm² removes all but 5 of the 406 particles (sizes in the range of 1 to 17 μm). Thus, this is a good estimate of the experimental critical fluence. Laser cleaning with lower-laser-pulse fluence removes (or reduces) a percentage of the particles. This percentage decreases with decreasing fluence (Fig. 7) and has a threshold for the onset of any removal of ~4–5 mJ/cm². The particle-size-resolved laser cleaning results (Fig. 8) show a trend for more effective removal of larger particles (>5 μm) and also possibly the 1-μm particles, where there is 100% removal at 51 and 103 mJ/cm². The experimental results are reasonably well described by the model of dome-shaped particles with a constant dome height. The experimental critical fluence of 220 mJ/cm² fits with a dome height of the order of 3 μm. The complete removal of 1-μm particles at 51 mJ/cm² is consistent with these smaller particles having a dome height of less than 1 μm. The earlier assumption that all of the incident laser energy is absorbed by the paraffin wax is supported by the fact that if anything, the predicted critical fluence is marginally high compared to the experiment. It is quite reasonable to expect the paraffin wax surface, with high roughness, will reflect little of the UV, and for all of the incident laser radiation to be completely absorbed in the hydrocarbon and none transmitted.

VIII. CONCLUSION

Paraffin wax domes have been successfully laser cleaned from glass microscope slides with the use of a single UV laser pulse. Almost complete removal was affected with a single pulse fluence of 218 mJ/cm². The process of removal by vaporization was initiated at a very low fluence of 4–5 mJ/cm² in the experiments. A theoretical model of the vaporization of spherical dome particles, where the domes are of the same height above the surface but of different radii, fits well with the experimental results for the particle sample preparation technique used. In contrast, a model of domes where the height is a constant factor of the radius predicts a critical fluence for removal which scales up with particle size. There is some evidence of the opposite trend in the experimental results.

Overall, the results suggest that particles of hydrocarbons, such as paraffin wax, can be successfully removed by laser cleaning when their height above the surface is up to of the order of their “radius.” Tall, small cross-sectional area “particles” of hydrocarbon represent a greater challenge and are to be avoided in real industrial situations. These results support modifying the use of waxes and thermopolymers as optical mountants to keep the layers used as thin as possible. This is in contrast with most of the manufacturers’ instructions which recommend liberal use of the mountant for mounting stability. There is a tradeoff to be met between stability during polishing/cutting and subsequent ease of total removal of the mountant, particularly for small-scale optics.

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