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Laser assisted cleaning: a comparative study of forward and reverse exposure

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This article is dedicated to Prof Pradeep K Gupta for his contributions to optics and photonics with biomedical applications

We report here on a comparative study of laser assisted forward and reverse cleaning techniques. Dye particulates simulated on LiF that is transparent to the incident laser radiation at 532 nm, served as the samples. Melting and partial ablation have been identified as the mechanisms of cleaning for low and high fluencies, respectively. Optical profilometric and microscopic probing of the laser exposed surface revealed a reduction in the height and increase in the base area of the contamination, respectively for both forward and reverse cleaning. The measurement of the total volume of contamination remnant on the exposed surface by employing the sensitive photo absorption technique established beyond doubt the decided advantage of reverse cleaning over forward cleaning.

Keywords: Laser assisted surface cleaning, Reverse cleaning, Optical profilometry, Photo absorption, Dye particulate contamination.

1 Introduction

Lasers have been, of late, recognised as efficient tools for surface decontamination in areas as diverse as semiconductor industry [1], heritage conservation [2], nuclear industry [3,4] etc. This is due to the fact that laser has the capability to expose the surface in both remote and controlled manner and to keep the volume of secondary waste to a minimum. The mechanism of removal in majority of the cases, depending on the laser parameters and contamination under consideration, may be thermo-elastic stress [5], ablation [6,7], shock [8,9] or spallation [10]. We have, in our earlier work, demonstrated and characterized efficient removal of translucent particulates from both metallic [11,12] and dielectric [12] substrates by taking advantage of laser induced thermo-elastic stress [5,13] and the same has been successfully applied to decontaminate radioactive surfaces [4,11]. The efficacy of laser in cleaning the surface without altering its properties, an essential prerequisite for application in nuclear industry or artwork conservation, was ascertained by employing thin layer activation technique [7,15]. Further, the enhanced field underneath a translucent particulate [13] has allowed us to generate microstructures on both metallic [15] and dielectric surfaces [16]. In majority of these applications, the laser beam impinges on the side of the surface that undergoes modification. There are, however, instances when a surface to be decontaminated is approachable only through the reverse side, e.g., the inner surface of a contaminated glove box where the laser cannot be placed in the first place, or a parchment of historic value where direct exposure may actually remove the ink etc. Although the literature is scarce, reverse cleaning, also referred to as verso cleaning, has nevertheless been tried in the past in case of thin

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mechanical films [17] and parchments of heritage value [9] with appreciable success. These two applications relied on the transfer of the thermo-elastic stress, generated due to the rapid rise of temperature following pulsed laser exposure, through the thin opaque substrate to the contamination on the other side leading to their expulsion. In this paper, we present the results on the advantage of verso cleaning over forward cleaning wherein dye particulates, deposited on Fused Silica substrate, served as the contamination while frequency doubled emission of an Nd-YAG laser operating at 532 nm wavelength served as the coherent source. The substrate being transparent to this wavelength, absorption of energy through the particulates is therefore, solely responsible for the generation of the cleaning force. While optical profilometry of the irradiated dye deposited samples did show evidence of reduction in the height of the particulates, to confirm the removal of dye from the surface, we also estimated the extent of cleaning in case of forward and reverse exposures by absorption spectroscopy. A clear advantage in cleaning of the dye contamination in case of reverse exposure was established.

2 Experiments, result and discussion

Samples were prepared by simulating contamination on fused silica substrates of optical grade surface finish (flatness λ/4 @ 632nm, 40-20 s/d) in the following manner. ~1 µl of Rhodamine B dissolved in acetone (at 0.57mM concentration) was deposited on the substrate surface over a diameter of ~5 mm and evaporated to dryness under an infrared lamp. The information with regard to the diameter of the particulates so formed was obtained through optical microscopy (Axio imager, Carl Zeiss make) while that related to their height was recorded by means of Optical profiler based imaging (Taylor Hobson Model CCI MP) before as well as after exposure to the laser radiation. Appropriate indentation on the sample surface allowed examination of a particular location of the sample both before and after its exposure to laser. The optical micrograph and optical profiler images of one of the deposited surfaces prior to laser exposure is as shown in Fig 1(a) and (b). ~91% of the particulates in this sample were estimated, by employing the axio imager software, to be within a diameter range of 3-8µm while the height of the majority of the particulates (~ 70%) was found to lie around 400 nm from the optical profilometer images. Schematic diagram of the experimental set-up is as shown in Fig 2 [12]. An Nd-YAG laser (SL332T, Ekspla), capable of delivering ~100mJ of

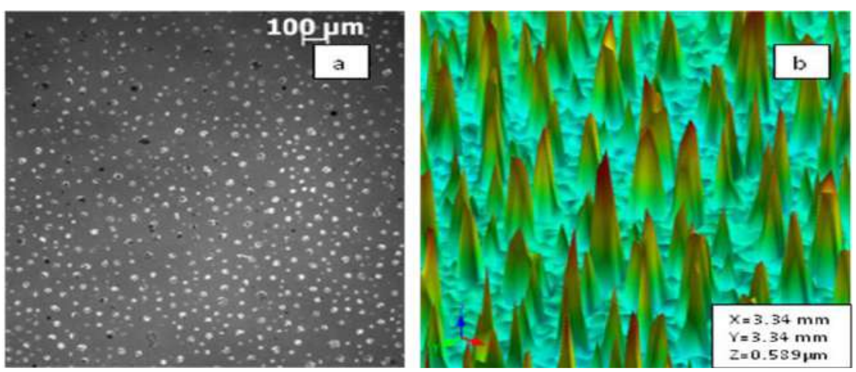


Fig 1. Typical images of deposited surface through (a) optical microscope (b) Optical profiler.

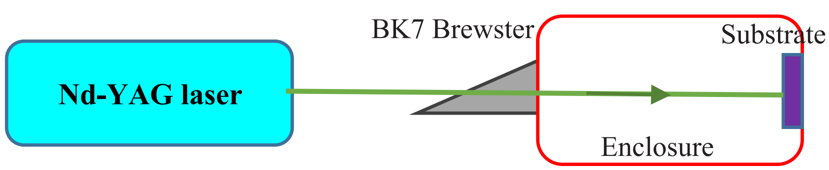


Fig 2. Schematic diagram of the experimental layout [12].

energy as a flat topped beam (8mm diameter) over a pulse of duration of 300 ps on 532 nm wavelength was employed as the coherent source. The sample was mounted on a sample holder that vacuum sealed a perspex chamber at one end while a BaF_2 Brewster window sealed its other end. This arrangement allowed exposure of the sample by the polarised laser beam without attenuation. In the first set of experiments, two samples were exposed to a single laser pulse of moderate fluence of ~30mJ/cm^2, one in the conventional forward direction, and the other in *verso*, meaning the laser beam reached the particulates through the transparent glass. To be noted here that the fluence in the reverse irradiation case will be correspondingly reduced due to the Fresnel reflection loss that the laser beam suffers at the two surfaces of the glass substrate before reaching the particulates. The Abbott-Firestone curves, that reveal the height of the particulates on the sample substrate, before and after laser irradiation, for both forward and reverse cases are as shown in Fig 3(a & b) and Fig 3 (c & d), respectively. In both the cases, the height of the majority of the particulates are found to be reduced by a factor of ~2. The temperature on the surface was estimated to be ~885K in the forward case and ~800 K in reverse case by making use of one dimensional heat equation [18]. The percentage absorption of the incident radiation in the dye particulates was estimated experimentally by comparing the energy of the

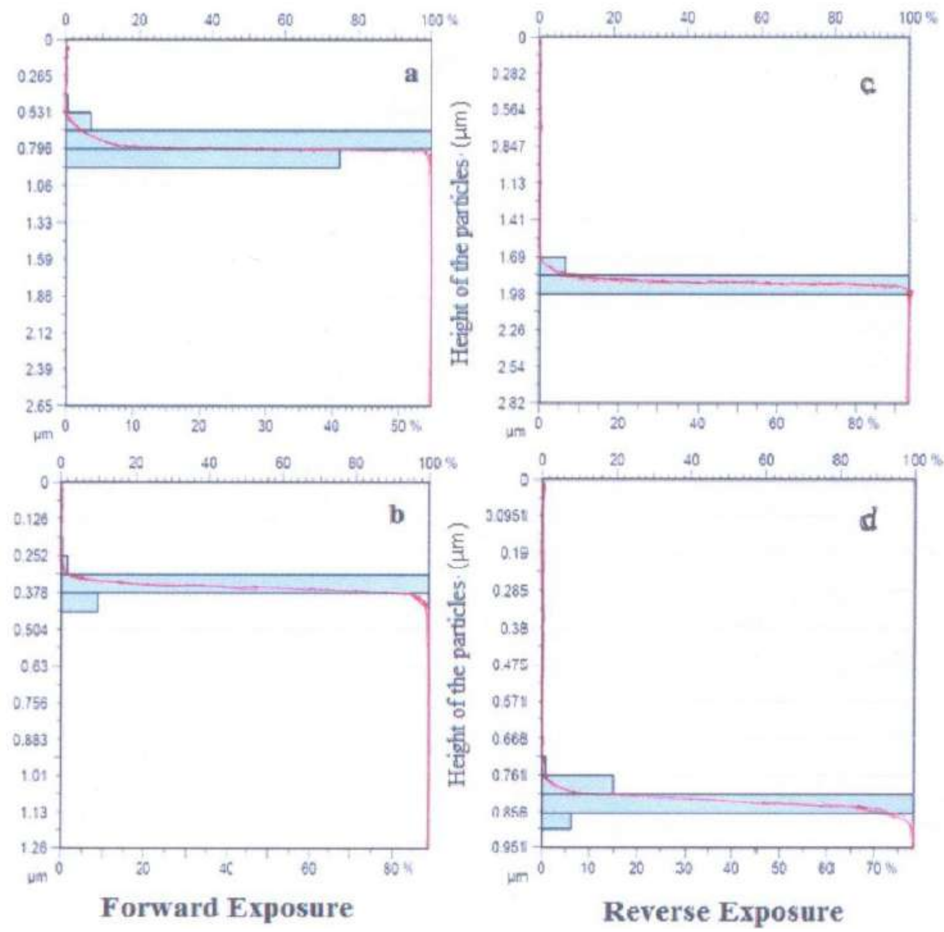


Fig 3. Abbott- Firestone curves depicting the height of the particulates before and after laser irradiation, (a & b) in case of forward exposure and (c & d) in case of reverse exposures, respectively at lower fluence. Upper horizontal scale in the curves indicates the % cumulative particulate number (shown as continuous red curve), while the lower scale indicates the % of particulates in the height range depicted by the histogram.

transmitted beam through contaminated and plain Fused Silica substrates and was found to be ~ 60% at 532 nm. As the melting and boiling points of Rhodamine B base are known to be ~520 K and ~910K, respectively, it is expected that the laser exposure will cause melting of the particulates under both forward and reverse cases. It is well known that with ps and fs laser exposures, heating effects are generally minimal. However, for our case, where the pulse duration is 300ps (sub ns duration), transfer of energy from the electrons to lattice does take place. As seen from the optical profiler image recorded in Fig 1(b), the particulates are predominantly conical with a sizable base. The melt from the top, in case of forward exposure, flows downward and resolidifies increasing, thereby, the base area of the particulates. In case of reverse exposure too melting occurs, however from the base, leading to once again an increase in the size of the particulates. The same is evident from the magnified microscopic images (Fig 4) of approximately the same location of the surface before and after exposure. This fact was further reconfirmed from the estimation of the area of the substrate surface covered by the contamination through microscope software. It is well known that spherical particulates, with a very small contact area with the substrate may be ejected due to thermo-elastic stress for laser fluence much less than what is needed for melting of the particulates [5]. However, if the contact area of the particulates with the substrate is substantial as it is in our case, the generated thermo-elastic stress might not exceed the minimum force necessary for the ejection of the particulates as a whole. Further, substrate being transparent, the transport of energy from the laser beam occurs through particulate absorption alone that is known to play a less dominant role in the process of cleaning [19]. The reduction in the height of the particulates (Fig 3) with almost no diminution in their numbers bears testimony to the fact that melting is responsible for the effect observed with laser exposure at this fluence level.

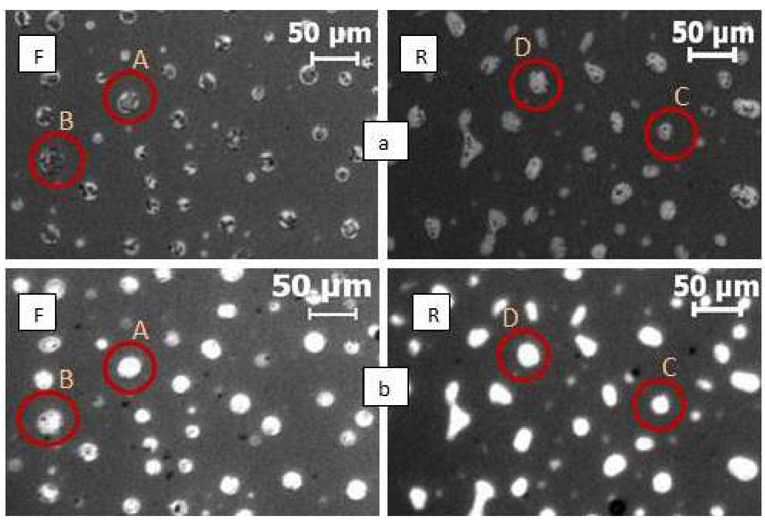
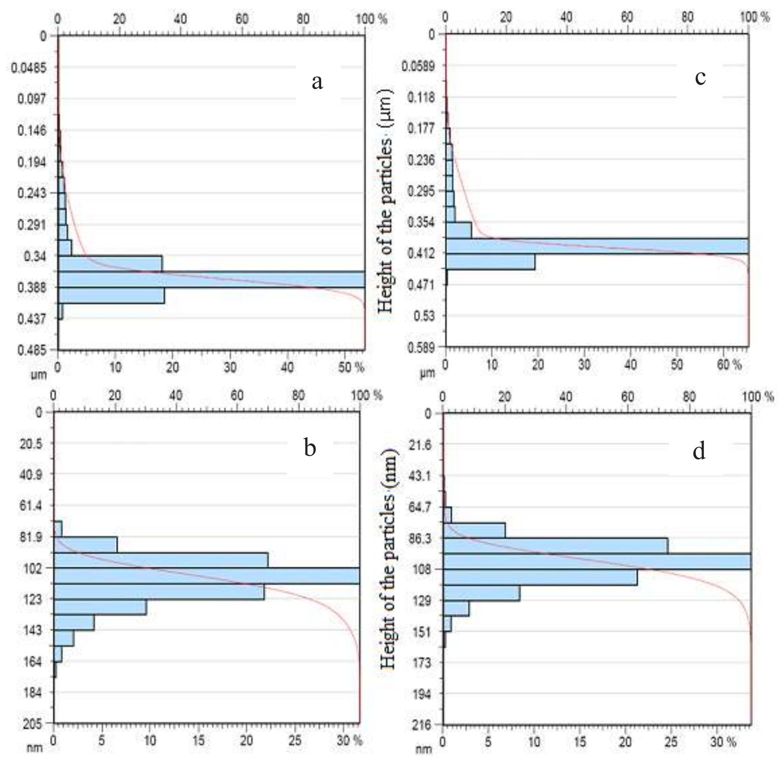


Fig 4. Optical micrographs showing the increase in particulate size following exposure to laser at low fluence, (a) before laser irradiation, (b) after laser irradiation (F-forward , R-reverse). The size of the particles A & B as measured by optical microscope were 23.3 µm and 25.7 µm prior to & 26.02 µm & 29.54 µm, respectively after the forward exposure, while the size of the particles C & D was 16.47 µm and 19.42 µm prior to & 17.07 µm & 20.71 µm, respectively after the reverse exposure.

In the next set of experiments two new samples were exposed to a higher fluence of ~120mJ/cm^2, once again in both forward and reverse directions. The Abbott- Firestone curves for these samples revealing the height distribution of the particulates prior to and after laser irradiation are shown in Fig 5. The reduction in the height of the majority of the particulates following the laser exposure is now seen to be almost 4 times in both cases. The surface temperature here was estimated in the same manner as before to be ~2435K for forward exposure and ~2137K for reverse exposure. The boiling point of rhodamine base being ~ 910K, ablation of particulates appears to be the most probable scenario here for both the cases. Substantial reduction in the number of particles present on the substrate surface following the laser exposure has been observed in both the cases although somewhat less for reverse cleaning (~38%) as against forward cleaning (45%). This is because the fluence in the forward direction is higher compared to reverse direction. However, it is interesting to note that while the area occupied by contamination following laser exposure reduced in both the cases, reduction is more for reverse cleaning (~45%) compared to forward cleaning (~30%). Careful examination showed that while the number of particulates in the 3-8μm diameter range showed a drastic reduction accompanied by a corresponding increase in 1-3μm range for reverse case, there is no such trend observed for forward cleaning (Fig 6 (a & b)). We attribute it to the fact that the partial ablation in case of reverse cleaning takes place from the base leading to an observable reduction in both diameter and height of the particulates. As is clearly evident from this figure, there is a removal of material under both irradiation conditions although it is not straight forward at this juncture to ascertain as to which mode of exposure has higher cleaning efficiency. Further, in case of reverse cleaning there is a possibility of particulate removal due to rapid ablation at the base causing a sudden upward thrust. Redeposition too is very likely in such a case.



Forward Exposure **Reverse Exposure**

Fig 5. Abbott- Firestone curves depicting the size of the particulates before and after laser irradiation in case of forward (a & b) and reverse (c & d) exposures, respectively at higher fluence. Axes are as described in Fig 3.

To quantify the extent of removal of the contamination and, in turn, ascertain the relative efficacies of forward and reverse cleaning, we made use of the sensitive method of absorption spectroscopy. ~2.5 μl Rhodamine B dye dissolved in water (at ~1.5mM concentration), taken in a micro-pipette was deposited in a micro-pipette on the substrate surface over a diameter of ~5mm and evaporated to dryness under an IR lamp. Since the absorbance measurements become erroneous for low concentration of the solution, to have adequate quantity on the surface even after laser exposure, the above process of deposition was repeated 4 times, meaning a total of ~10 µl was deposited on the substrate surface. Water was used as the medium for preparing solution as it allowed the deposition to remain confined to a smaller area. This was essential to ensure complete overlap of the laser beam with the deposited contamination while keeping the concentration high at the same time. From the samples so prepared, 4 samples were randomly picked and the absorbance measurement in the contamination deposited on them was carried out in the following manner: Using 2 ml of acetone in a micropipette, the entire contamination was carefully collected into a cuvette and was placed inside the spectrophotometer and its absorbance was measured. This measured absorbance is directly proportional to the concentration of Rhodamine B. The nearly equal values of absorbance measured for all the four samples (1.12 ±0.02) indicate the accuracy of the sample preparation.

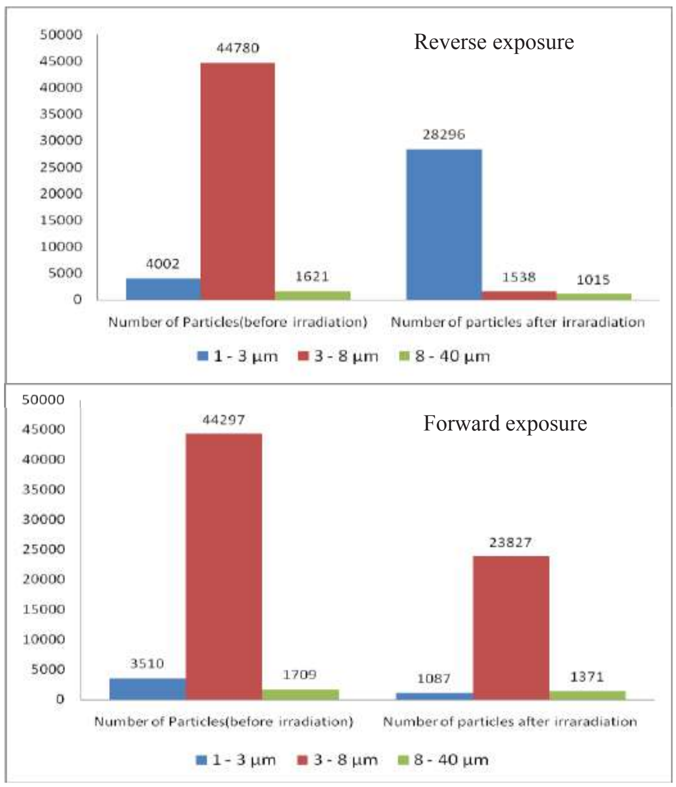


Fig 6. Histograms depicting number of particulates, categorised on the basis of their sizes, before and after laser irradiation for both reverse and forward exposures.

We then quantified the cleaning for both forward and reverse exposures for two fluence conditions, high (~160 mJ/cm^2) and low (~30 mJ/cm^2), but both capable of causing ablation. For each fluence, three samples were exposed and analysed to minimize the error. To be noted here that the fluence in the reverse irradiation case will be correspondingly reduced due to the Fresnel reflection loss as stated before. The absorbance measured for the forward and reverse cases before and after irradiation is shown in Fig 7. This clearly indicates a definite cleaning in case of both forward and reverse exposures while the efficiency is seen to be considerably higher for reverse exposure. For exposure to the higher fluence too (~ 160 mJ/cm^2), similar trend was observed but with a higher material removal. The change in absorbance, and in turn particulate concentration on the substrate surface, as a function of laser fluence for forward and reverse exposures is depicted in Fig 8.

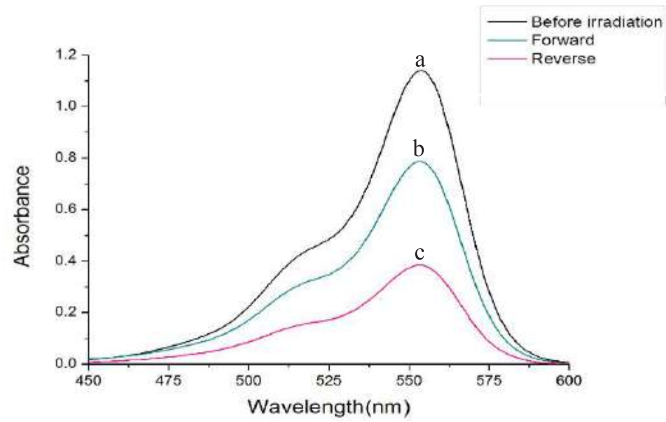


Fig 7. Absorbance as a function of wavelength at a fluence of ~30mJ/cm^2 for all the three cases a. Before exposure, b. Forward exposure and c. Reverse exposure.

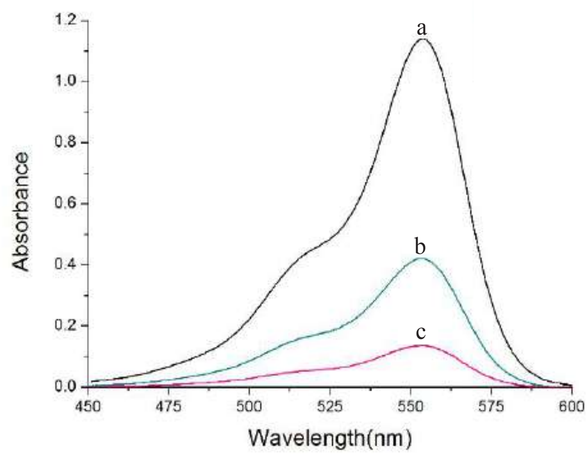


Fig 8. Absorbance as a function of wavelength at a fluence of ~160mJ/cm^2 for all the three cases; (a) Before exposure, (b) Forward and (c) Reverse.

4 Conclusion

In conclusion, the cleaning efficiency is always found to be higher for reverse exposure (~88% for the highest fluence) as compared to forward (~62%) even though the fluence is lower due to Fresnel reflection losses in the reverse case. This can be understood qualitatively in the following manner. In case of reverse cleaning, the thermal stress or the ablation process is initiated from the particulates that are in immediate contact with the substrate surface. The expanding vapour imparts an upward thrust to the particulates atop thereby facilitating the process of cleaning. In case of forward exposure, on the other hand, the ablation/expulsion is initiated from the top and the expelled material simply gets out. Using a gas jet can enhance the cleaning efficiency in both the cases in particular for forward cleaning wherein redeposition too can play a significant role.

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