Laser Processing of Poly(methyl methacrylate) Lambertian Diffusers

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Abstract

Matrix-assisted pulsed laser deposition was used to deposit poly(methyl methacrylate) on silicon wafers and sodium silicate glass slides for the purpose of making optical diffusers. After deposition, the reflectance of the coated substrates was measured as a function of scattering angle. We found that the angular dependence of the reflectance could be described as the sum of two functions. First, a Gaussian describes the specular reflection of the underlying substrate that has been broadened by passage through the film. Second, a cosine function describes the reflectance contribution from the film itself. We found that by increasing the thickness of the deposited film that we could eliminate the specular reflection to obtain Lambertian diffusers. Since we can control the surface roughness by adjusting the ratio of the two matrices in laser-processing, this deposition technique offers the possibility of producing a wide range of diffusers of different types.

1 Introduction

Diffusers are important optical elements that can be used to improve lighting in photography[1], to protect sensitive optical elements from damage[2], and to control lighting in display applications[3]. A diffuser is characterized by its ability to effectively distribute radiant energy from an incident source in the far field. As a specific example, a reflecting Lambertian diffuser follows a cosine law for the irradiance, and thus appears the same regardless of viewing angle.

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14. ABSTRACT

Matrix-assisted pulsed laser deposition was used to deposit poly(methyl methacrylate) on silicon wafers and sodium silicate glass slides for the purpose of making optical di users. After deposition, the re ectance of the coated substrates was measured as a function of scattering angle. We found that the angular dependence of the re ectance could be de- scribed as the sum of two functions. First, a Gaussian describes the specular re ection of the underlying substrate that has been broadened by passage through the lm. Second, a cosine function describes the re ectance contribution from the lm itself. We found that by increasing the thickness of the deposited lm that we could eliminate the specular re ection to obtain Lambertian di users. Since we can control the surface roughness by adjusting the ratio of the two matrices in laser-processing, this deposition technique o ers the possibility of producing a wide range of di users of di erent types.

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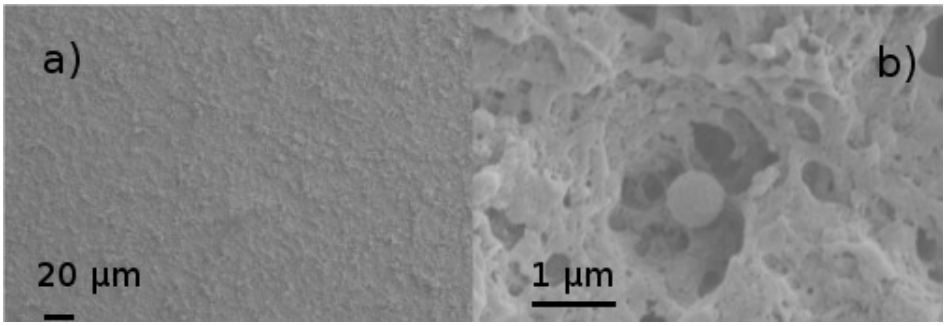

Figure 1: SEM micrographs of PMMA deposited on Si wafers. These are typical of the films used in this study. In (b) we see a polymer spheroid that appears frequently in these films.

We have fabricated diffusers using matrix-assisted pulsed laser deposition[4] in which a resonant infrared laser is utilized[5]. In this technique, the material to be deposited (guest) is dissolved in an appropriate solvent (matrix, host) and the solution is frozen and then placed in a vacuum chamber. A focused pulsed laser is incident upon the target and the resulting plume is intercepted by a substrate where a thin film collects. Recent results indicate that the surface roughness of the deposited films may be controlled in the range of roughly 30 nm to 1000 nm by adjusting the composition of the matrix[6]. We have utilized this feature to deposit rough polymer films that readily diffuse incident 532 nm CW laser light.

2 Results and Discussion

The matrices used in this study were binary mixtures of methanol and toluene, in the ratios 80M:20T or 90M:10T by weight unless otherwise indicated. The deposited polymer was poly(methyl methacrylate) (PMMA), chosen for its wide applicability and good optical properties in the visible and near-UV. Neither methanol nor toluene is a good solvent for PMMA, but mixed in the right ratios, these two miscible solvents are very effective in dissolving the polymer[7]. However, in this study, mixtures that were poor solvents were deliberately chosen to facilitate the deposition of rough films on glass and silicon substrates[6]. A free-running Er:YAG laser (2937 nm, 350 μs) was used for the deposition and the fluence was 3.1 $\frac{J}{cm^2}$. The repetition rate was 10 Hz and the spot size was approximately 0.04 cm^2. The beam was rastered by a computer-controlled mirror and the target was rotated at about 0.5 Hz. Prior to each deposition, the chamber was evacuated to a base pressure of about 1 *Pa*. The total film thickness is estimated to be about 1.5 - 2 μm, based upon earlier measurements where we obtained a deposition rate of 50-60 nm/minute with similar conditions.

Readers who are more familiar with UV-MAPLE may find the fluence used in the deposition experiments to be somewhat high as typical values in UV-MAPLE are about one to two orders of magnitude lower. However, since we are using an mid-IR laser, we can expect the absorption coefficient to be about one or two orders of magnitude smaller than that which is characteristic of the UV. In MAPLE, the nature and quality of the deposited films often depend directly on the energy per unit volume[8], or the product of fluence and absorption coefficient. Therefore, since infrared absorption coefficients are much smaller in the IR than the UV, we can expect the laser

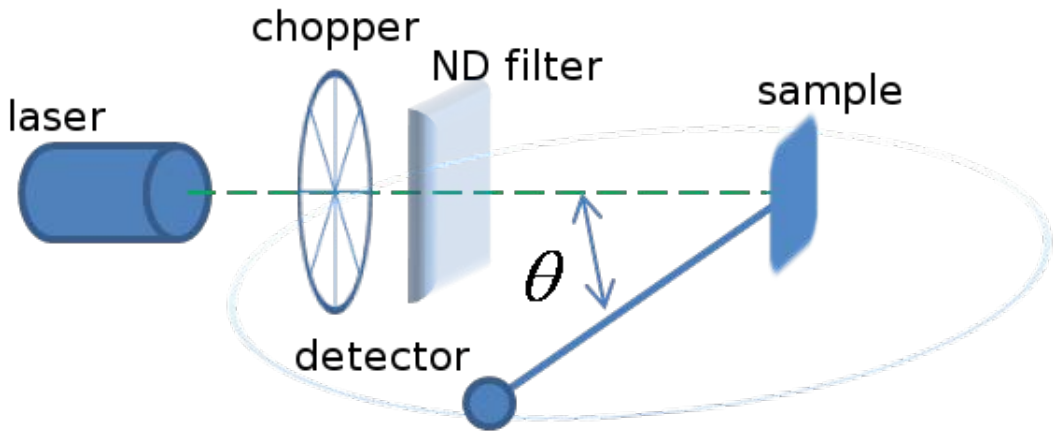

Figure 2: Simplified schematic of scattering experiment.

fluence to be correspondingly larger.

Scanning electron micrographs of films deposited using 90M:10T solvent mixtures are displayed in Fig. 1. Similar images for a 80M:20T matrix may be found in Ref [6]. The surfaces are very rough and have been measured by atomic force microscopy to be in the range of 500-600 nm (RMS). For our scattering measurements, a simple reflectometer was constructed and is shown in Fig. 2. A 100 mW CW 532 nm laser beam was chopped (Stanford SR 540) and attenuated by a neutral density filter (17 mW) and was normally incident upon the diffuser. Films that were deposited on silicon reflected and scattered all of the incident radiation back into the half-space that contained the optics. A Thorlabs DET 110 photodiode was used to monitor the relectance as a function of angle. A computer-controlled rotation stage was used to adjust the position of the detector and the output was fed into a Stanford SR830 DSP lock in amplifier. The equipment was interfaced through National Instruments LabView software and the data acqusition was automated.

A typical scattering result is displayed in Fig. 3a. Two distinct contributions to the reflectance are evident as is described in Ref [9]. One is described by a Gaussian function centered on 0 degrees and the other by a Cosine. The line in Fig. 3 is a fit to a composite reflectance function that has the form:

$$R(\theta) = Ae^{-(\frac{\theta}{\theta_0})^2} + B\cos(\theta). \tag{1}$$

The first term is due to the specular reflection from the underlying substrate that is broadened due to passage through the film. The second term arises from reflection off of the surface of the rough film and is associated with a Lambertian diffuser, i.e. a surface that appears the same independent of viewing angle. The ratio of these two terms depends on the thickness and, as shown in Fig. 3b, for thick films the Gaussian term disappears, leaving only the Cosine term. In this case, the film has become thick enough to eliminate the specular reflection from the underlying substrate entirely. Here, the film was deposited in 4 parts and the scattering measurement was performed after each one. The first two segments were 10 minutes long, while the third was 6 minutes and the fourth four minutes long for a total deposition time of 30 minutes.

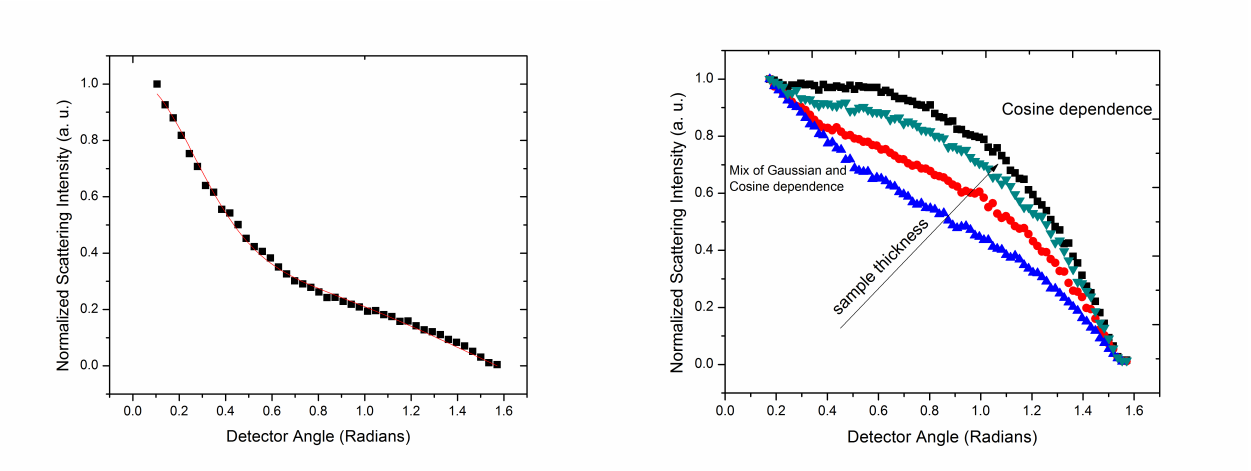

Figure 3: (a) Typical result for deposited film with fit to composite reflectance function (Eqn. 1) and (b) evolution of reflectance with sample thickness for PMMA film deposited upon Si (100) substrate. In (a) the fitting coefficients A and B are 0.387 ± 0.006 and 0.630 ± 0.01 respectively. In (b), for the rightmost curve $A = 0$.

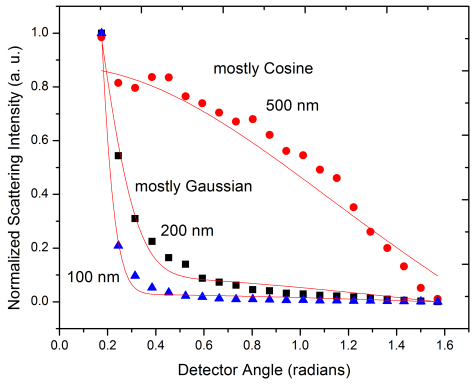

Figure 4: Reflectance for three films. Film 1 (100 nm RMS roughness) is PMMA deposited from a 50M:50T matrix. Film 2 is PEG deposited using a methanol matrix (200 nm RMS roughness). Film 3 is PMMA deposited using an 80M:20T matrix (500 nm RMA roughness).

In addition to altering the reflectance by increasing the film thickness, we can control the surface roughness, and by extension the reflectance, with the selection of both the guest materials and/or the host. In Fig. 4, we show the reflectance for three different films of similar thickness (~300 nm). The first has a surface roughness of about 100 nm and is deposited from a 50M:50T matrix with 1% PMMA by weight. Second is a polyethylene glycol film deposited from a methanol matrix (2 wt % PEG) with a surface roughness of about 200 nm. Finally, the last film is deposited using an 80M:20T matrix (1 wt% PMMA) and has a roughness of about 500 nm. This figure shows that it is possible to use other materials for the films and to target different reflectance profiles by altering the matrix composition with PMMA.

3 Conclusion

Thin films of PMMA deposited by matrix-assisted pulsed laser evaporation have been characterized for their use as optical diffusers. By controlling the thickness and surface roughness of the films, they could be tailored with the properties of a Lambertian diffuser. As studies with other polymers deposited by this technique have also shown the ability to control their thickness and surface roughness by careful choice of solvent/guest pairings and laser energy, we believe this to be a general process not limited to PMMA.

References

[1] Stephen Wadle; Daniel Wuest; John Cantalupo; Roderic S. Lakes. Holographic diffusers. *Optical Engineering*, 33(01):213–218, 1994.

[2] Stephen A. Burns and Robert H. Webb. Optical generation of the visual stimulus. In *Handbook of Optics, Volume III*, page 5.21. McGraw Hill Professional, New York, N. Y., 2009.

[3] Tasso R. M. Sales, Stephen Chakmakjian, G. Michael Morris, and Donald J. Schertler. Light tamers: Engineered microlens arrays provide new control for display and lighting applications. *Photonics Spectra*, 38(6), 2004.

[4] D. B. Chrisey, A. Pique, R. A. McGill, J. S. Horwitz, B. R. Ringeisen, D. M. Bubb, and P. K. Wu. Laser deposition of polymer and biomaterial films. *Chemical Reviews*, 103(2):553–576, 2003.

[5] D. M. Bubb, S. M. O'Malley, C. Antonacci, D. Simonson, and R. A. McGill. Matrix-assisted laser deposition of a sorbent oligomer using an infrared laser. *Journal of Applied Physics*, 95(4):2175–2177, 2004.

[6] D. M. Bubb, Michael Papantonakis, Brian Collins, Elijah Brookes, Joshua Wood, and Ullas Gurudas. The influence of solvent parameters upon the surface roughness of matrix assisted laser deposited thin polymer films. *Chemical Physics Letters*, 448(4-6):194–197, 2007.

[7] Charles Hansen. *Hansen Solubility Parameters: A User Handbook*. CRC Press, Boca Raton, Fl., 2000.

[8] Daniel M. Bubb, Jeff Corgan, SunYong Yi, Mishae Khan, Leon Hughes, Ullas Gurudas, Michael Papantonakis, and R. Andrew McGill. An experimental investigation of inhomogeneities in resonant infrared matrix-assisted pulsed laser deposited thin polymer films. *accepted for publication, Applied Physics A: Materials Science and Processing*, 2010.

[9] Peter Hannson. *Surface Characterization using Radiometric and Fourier Optical Methods*. PhD thesis, Uppsala University, Uppsala, Sweden.