Optical properties study of silicone polymer PDMS substrate surfaces modified by plasma treatment

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Abstract

In this study, PDMS (polydimethylsiloxane) substrates with a half-plain, half-rough surface were prepared on a plain and rough fused silica glass substrate using a molding technique. The molded PDMS surface morphology was changed into a half-smooth and half-rough surface after peeling. The modified PDMS surfaces’ optical properties were inspected with and without treatment. The treatment is exposed by oxygen plasma (15 W) for 3 min in a vacuum, down to a pressure of six torr, using a vacuum pump. An atomic force microscope (AFM) and interferometer (white light) indicated that the plasma O2 treatment increased the formation of the plain surface and decreased the formation of the rough surface. The optical properties via a spectrophotometer (lambda) show the resonance from 300 nm to 1200 nm on the rough surface, which is considered to be a faithful reproduction for transmittance and reflectance. The Raman spectra and FDTD simulation results are in excellent agreement; not to be confused with metal local surface plasmon resonances (LSPRs). The Raman spectra peaks and hotspot are the results of the PDMS Si–O backbone. The PDMS substrate presented the diversity of the optical properties, which makes the substrate complementary to various optical applications.
2. Materials and methods

The PDMS half-rough and half-plain surface is prepared by the following method, as illustrated in figure 1. In the above steps, we take the fused silica glass slide (7 $\times$ 5 $\times$ 2 mm$^3$). The glass slide has two equal sections, half-rough (or frosted) surface and half-plain surface, and each section has a dimension of (3 $\times$ 4 $\times$ 2 mm$^3$). First, the fused silica glass and then the PMMA frame (6 $\times$ 4 $\times$ 3 mm$^3$) were installed into a rectangular petri dish, respectively. The Sylgard 184 silicone elastomer kit (Dow Corning Corporation) by weight ratio with a base-curing agent (10:1) are mixed in disposable glass, stirred for 5–8 min at ambient temperature and dispensed on the master fused silica glass slide, which is installed on the rectangular petri dish. Next, the bubbles are removed after 15 min in a vacuum chamber, followed by curing at 65 °C for 4 h. The stripped-down PDMS substrate from the fused silica glass slide and PMMA frame have a thickness of 2 mm, which is measured by a Vernier caliper scale. Hereby, under the same conditions, we prepared two PDMS substrate samples. Each sample has two portions, namely a half-plain surface and half-rough surface. Afterwards, one PDMS substrate sample was treated by O$_2$ plasma that has a half-plain and half-rough surface under the conditions of 15 W for 3 min, while the other half-plain and half-rough surface sample was left untreated for comparison. Finally, the PDMS substrates are ready for measurements at room temperature.

Before going further, the PDMS substrates are characterized by different tests. Firstly, both of the PDMS substrates, as a reference with the master rough and plain fused silica glass substrate, are tested by a UV–Vis–NIR double-beam spectrophotometer (Lambda 1050, Perkin-Elmer). The transmittance, reflectance and absorption spectra are shown in figure 2, respectively. Secondly, the surface roughness is examined by atomic force microscopy AFM (XE-100, Park Systems) with a scanning area of 3 $\mu$m $\times$ 3 $\mu$m, as illustrated in figure 3. Thirdly, the $R_q$ values (root-mean-square surface roughness) are also observed and calculated by the white light interferometer (Nano GmbH), as shown in figure 4. Fourthly, the Raman test is conducted by Renishaw’s inVia Raman microscopes (JPK instruments), as shown in figure 5. Finally, the commercial software FDTD is employed to calculate the electronic field distribution of PDMS substrates with a countless degree of surface roughness.

3. Results and discussion

To characterize the modified PDMS structure, the optical properties of plain and rough surfaces before and after plasma are measured by a UV–Vis–NIR double-beam spectrophotometer (Lambda 1050, Perkin-Elmer). The transmittance, reflectance and absorption spectra are shown in figure 2, respectively. Firstly, a spectra comparison was made for transmittance between the master fused silica glass substrate and replica PDMS substrate, both of the substrates’ plain and rough surfaces are shown in figure 2(a). A high transmittance on the PDMS substrate in a visible light domain is attained. In comparison, the transmittance of the plain PDMS substrate is 95%, and that of the fused silica glass is 90%, which leads the PDMS transmittance to be 5% better than the fused silica glass. Respectively, on the PDMS rough side transmittance is 92% and the fused silica glass is 75%. Here the PDMS rough substrate transmittance is 17% better than the rough fused silica glass substrate, showing that PDMS is a reasonable alternative on both surfaces instead of the fused silica substrate. Further study reveals that by altering the side of both the rough substrates the transmission spectra is going to weaken, such as the rough back side of PDMS has 80% transmittance and the fused silica glass has 70% transmittance. The results show that the roughness modification with the same material on a plain substrate is in good agreement with the transmission spectra. Secondly, the spectra comparison made for reflectance between the master fused silica glass’s plain and rough substrate and replica PDMS plain and rough substrate is shown in figure 2(b). The reflectance of the PDMS plain substrate is 7.5% to 6.5% and the fused silica plain glass is 12% to 10.5% in a 300 nm–1200 nm wavelength range, which means that the fused silica glass reflectance is better than the PDMS substrate. The rough side PDMS reflectance is 12%–3% also having resonance, while the fused silica rough glass reflectance is 12%–8%. Hereinafter, within the range of 300 nm–1200 nm, the PDMS and fused silica rough substrate may have
Figure 1. The fabrication process schematic diagram of the PDMS substrate.

Figure 2. The fused silica glass and PDMS spectra for plain and rough surfaces (a) transmittance (b) reflectance and (c) absorption.
Figure 3. AFM images (a) plain surface (b) plain surface after plasma treatment (c) rough surface (d) rough surface after plasma treatment.

Figure 4. White light interferometer images (a) plain surface (b) plain surface after plasma (c) rough surface (d) rough surface after plasma.
found a promising application in GMRF, concave and convex lenses domain. Further study on the reflectance realm revealed that the back side of the rough substrate increases the reflectance on different wavelengths within the range of 300 nm–1200 nm. The rough back side of PDMS reflectance is 17%–7%, and also has some peaks. Besides, fused silica glass is 16%–4%, which proves that the PDMS rough substrate back side reflectance is better because the reflected rays, after touching the handiness of the rough surface, scattered back through the PDMS surface. This boosting effect is under consideration for our future research using PDMS as an efficiency booster.

Thirdly, the spectra comparison made for absorption between the master fused silica glass plain and rough substrate and replica PDMS plain and rough substrate is shown in figure 2(c). The PDMS plain substrate has peaks at 1150 nm, as well as minor peaks at 850 nm, 900 nm and 1020 nm. Accordingly, the plain fused silica glass has a tiny peak at 820 nm. Next, the rough PDMS surface has different resonance peaks from 300 nm to 1200 nm and the highest peaks were observed at 350 nm and 820 nm. The fused silica rough glass has a minor peak at 820 nm. The rough surface PDMS back side has almost the same peak pattern but high absorption is detected. The continuous high and low peaks between the color spectrum range are shown in figure 2(c). Therefore, the stronger field scattering and significant enhancement in the rough surface make the PDMS potentially useful as a replica, low-cost, high-active substrate for optical applications such as solar energy.

In the literature, various post-processing treatments are used for PDMS substrates to improve the hydrophilic properties, in which the plasma O$_2$ treatment is the simplest technique. For the reasons of better understanding and comparing the surface morphology, O$_2$ plasma treatment is considered in this attempt. The plain and rough surfaces before plasma and after plasma are examined via atomic force microscopy (AFM), as shown in figure 3. The plain surfaces before plasma are shown in figure 3(a), and after plasma in figure 3(b). The rough surfaces before plasma are shown in figure 3(c) and after plasma in figure 3(d). The $R_q$ values of the PDMS samples are explained in figure 3. The $R_q$ values of the plain surface before and after plasma and the rough surface before and after plasma are 1.441 nm, 40.031 nm, 3.753 nm and 40.377 nm, respectively. After the plasma treatment, a significant influence on the rough surface is observed due to the substrate roughness; with the roughness of the PDMS substrate rising up to a maximum value of the rough substrate and then again increasing with further increments. Furthermore, the plain and rough surfaces have same tendency to vary before and after plasma. The tendency noted here was also under consideration for polymers or PDMS [19, 20]. During the peeling process the surface roughness depends on the bonding between the replica PDMS substrate and master fused silica glass substrate, which varies on both sides for properties (replica and master) such as temperature, geometry, size, density, among others [19]. The subjected plasma substrate roughness at some maxima becomes constant and has negligible influence on the PDMS substrate. We also observed insignificant influences on the substrate ratios.

Moreover, the surface of the PDMS is hydrophobic and the O$_2$ plasma thickness for the PDMS plain surface with a different treatment time is well known. Accordingly, the eigenvalue equation for resonance [22], by a minor change in substrate thickness, leads to a change in the optical properties or resonance wavelength. But, in our case the required rate of change in the thickness of the substrates’ surfaces are different, which varies in a different manner for the plain and rough substrate surface. The thickness of both the plain and rough substrate surfaces are illustrated in figure 3. The thickness of the plain surface before and after plasma is 46.815 nm and
165.568 nm, respectively, which shows an incremental rise in thickness. The thickness of the rough surface before and after plasma is 55.713 nm and 153.346 nm, respectively. By investigating the basic optical properties of the PDMS plain and rough surface it is clear from the results that the rate of change of thickness for both substrates is different; such as the plain surface increasing to some value and the rough surface decreasing to the roughness level and again increasing to some maximum value.

Furthermore, the $R_q$ values are also observed before and after plasma for the plain and rough surfaces with a white light interferometer, as shown in figure 4. The plain surface before plasma is shown in figure 4(a) and after plasma in figure 4(b). The rough surface before plasma is shown in figure 4(c) and after plasma in figure 4(d). Each substrate has $R_q$ values of 0.148 nm, 0.130 nm, 0.156 nm and 0.132 nm. The obtained values on the plain and rough surface have an influence on the decrease after plasma treatment. Less influence is observed on the rough surface because the rough substrate already has a rough surface. After treatment, the rough substrate first reached its maximum roughness level; during which it shows a decrement in roughness but after reaching the maximum values of the rough substrate it again starts to show an incremental rise on the substrate. This is a good match to an existing theory [21]. Because of the material softness and unavailability of Plasmon’s resonance and the material’s dielectric nature, equipment hardly focuses on the rough surface before and after plasma. Moreover, the material properties were changed after O$_2$ plasma treatment, causing thickness and refractive index change. The thickness results measured by AFM are illustrated in figure 3 and the refractive index properties are obtained from the figure 2 results. The enhancement results of the PDMS substrates reduced the optical properties such as transmittance.

Figure 5 shows the Raman spectra of the plain and rough surface before and after plasma treatment. Firstly, the Raman spectra map on to the plain surfaces are shown in figures 5(a) and (b). Both plain surfaces have peaks on the same range, the first and highest peak was observed at 450 nm, the second at 650 nm, the third at 600 nm and two small peaks were also observed at 1250 nm and 1410 nm. In comparison, the plasma-treated plain surface has a negligible increment in peaks which means that the signal intensities were improved significantly. Both rough surfaces before and after plasma treatment are shown in figures 5(c) and (d). The peaks are also observed in same range and manner. If a comparison is made between both the plain and rough surface before plasma shown in figures 5(a) and (c), the intensity starts to decrease. After plasma treatment both the plain and rough surfaces shown in figures 5(b) and (d) move towards an incremental rise; this means that both surfaces have a reverse relationship. Furthermore, on plain surfaces after plasma treatment negligible increase was observed in the peaks. On the rough surface a more significant increment was observed compared to the plain surface. The signal intensities were improved significantly, as shown in figure 5(d). These results clearly proved the enhancement theory, which means that the rough surface after plasma treatment will improve the intensity up to some maximum value of roughness and again moving towards a decrement. Moreover, the peaks on the PDMS substrates are not due to the metal’s Plasmon’s resonance, it’s due to the Si–O backbone of PDMS. The proposed PDMS substrate shows a favorable application in optical communication and could be used as an alternative to glass substrates.

As an application demonstration, the Raman scattering spectra of Rh B molecules on PDMS plain and rough surface films after plasma treatment are shown in figure 6. Both the plain and rough surfaces were used as SERS substrates for probing rhodamine B (Rh B) molecules (concentration = 0.1 µm). The Rh B molecule solutions were dosed on to the PDMS film’s surface. The Rh B is a typical artificial dye that we used as a test compound for PDMS films to detect trace toxic organic compounds. Figure 6(a) shows the detected SERS spectra of the Rh B molecules on the plasma-treated plain surface and figure 6(b) shows the spectrum of the plasma-treated rough surface. According to figure 6, the signal intensity increases on the rough surface, with enhanced intensity according to its surface roughness. The same types of enhancement are also emerging in practice for metal surfaces named SERS (surface enhancement Raman scattering). Although our practical results were evidenced due to the Si–O backbone of PDMS, we can also show this type of enhancement on PDMS substrates, which was practically observed for the first time. Eventually, this attempt certified that the roughness enhances the intensity while the substrate is PDMS. The strong Raman bands at different frequencies (cm$^{-1}$) are shown in figure 6. Therefore, the practice PDMS films have great potential to be used as a replica, low-cost, high-performance active substrate for SERS as well as other applications.

Finally, the commercial software FDTD (finite-difference time domain) is employed to calculate the electronic field distribution on both the rough and plain surface of the PDMS substrate. The calculated E-field intensity spatial distributions on both the PDMS substrate before and after plasma with various degrees of surface roughness are shown in figure 7. In design, the 470 nm laser illuminates perpendicularly to the ($x$–$y$) plane of the PDMS substrate with the polarization direction along the $y$-axis. When the PDMS substrate is smooth, the electric field distribution intensity decreases, as shown in figure 7(a). After the plasma treatment the PDMS substrate roughness increases; the intensity of the electric field rises and the dispersal regularity of the free electron concentration shows a tendency to increase, as shown in figure 7(b). On the other hand, the rough PDMS surfaces before and after plasma treatment are shown in figures 7(c) and (d), respectively. The intensity of the electric
field rises on the rough surface more than the plain surface, as shown in figures 7(a) and (c). On the rough surface after plasma treatment, the dispersal regularity of the free electron concentration shows a tendency to decrease. Moreover, one can easily make a comparison from figure 7 or from the ‘hot spots’ illustration. According to the electromagnetic enhancement theory, the substrate surface roughness induces after enhancement or treatment and as a result has hot spots or tilts. Moreover, the simulation result shows that the rough surface without plasma treatment makes a major contribution to enhancing the electric field, due to the availability of the high-density hot spots. In fact, this respective enhancement occurs due to the PDMS Si–O backbone [12], not because of the metal particles. The FDTD simulation calculation can be reasonably evaluated with the experimental results.

4. Conclusions

In this study, the optical properties of PDMS substrates with a half-rough and half-plain surface, with and without plasma treatment, were analyzed and compared experimentally and numerically. The results showed that the PDMS substrate presents a diversity of optical properties. The preferential orientation and surface roughness
have the same tendency towards variation on the substrates but opposite behaviour. The plain surface roughness has a tendency to increase and the rough surface to decrease up to a maximum surface roughness value. The primary discovery of our experiment for the first time revealed the relevance of the substrates’ surface roughness and post-processing techniques, which has no major influence whether the surface is rough or plain; because when the substrate surface is rough, after post-processing the roughness decreases, likewise if the substrate surface is plain, after post-processing its roughness shows an increase. Somehow, at some maximum point, both the plain and rough substrate surfaces will obtain the same roughness. The optical transmittance, reflectance, and absorption show good agreement with the same material modification, such as after peeling from the master rough and plain surface, the same pattern transfers on to the PDMS substrate without any enhancement. The Raman scattering raised with plasma treatment on both the rough and plain surface in an opposite manner decreases with more increasing. This occurs due to the variation of the Si–O backbone. The Raman recorded spectra of the Rh B molecule on both surfaces defines the Raman scattering enhancement ability. Finally, the significant enhancement in the rough surface, reasonable field scattering and transmittance make PDMS of great potential to be used as a replica, low-cost, high-active substrate for optical applications such as solar energy.

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References

[1] Rittenhouse D 1786 Trans. Am. Phil. Soc. 2 37–42
[2] Matthias G et al 2009 J. Phys. Chem. C 113 17296–300
[3] Kou Q et al 2004 Microelectron. Eng. 73 876–80
[4] Sulchek T et al 2000 Rev. Sci. Instrum. 71 2097–9
[5] Jo B H, Van Lerberghe L M, Motsegood K M and Beebe D J 2000 J. Microelectromech. Syst. 9 76–81
[6] Markel V A et al 1999 Phys. Rev. B 59 10903–9
[7] Yuksel T, Robert D L, Govind V K and Emmanuel D 2015 Microelectron. Eng. 132 156–75
[8] Jinwen Z, Amanda V E and Nicolas H V 2010 J. Nanosci. Nanotechnol. 10 1–5
[9] Changshou P et al 2010 Opt. Express 18 24753–61
[10] Martin A, Sebastian S and Stefan S 2010 Opt. Lett. 49 4326–30
[11] Dong X L et al 2015 J. Mater. Chem. C 3 1751–6
[12] Anne L S et al 2016 Dielectric Elastomers (DEs) as EAPs: Materials (Berlin: Springer) (https://doi.org/10.1007/978-3-319-31767-0_31–1)
[13] Shinji D, Junya H, Sho Y and Tsubasa S M 2015 J. Micromech. Microeng. 25 097002
[14] Wolfgang A C B et al 2010 Lab Chip 10 1814–9
[15] Jordi V P, Stefanie D, Stephanus B and Andreu L 2012 Opt. Pura Apl. 45 209–13
[16] Daw R and Finkelstein I 2006 Nature 442 367–418
[17] Zhao Z et al 2008 J. Clin. Microbiol. 46 3752–8
[18] Forrest S R 2004 Nature 428 911–8
[19] Boyin L and Jing F 2015 J. Micromech. Microeng. 25 065006
[20] Bolbach G et al 1988 Nucl. Instrum. Methods Phys. Res. B 30 74–82
[21] Karim S et al 2006 Appl. Phys. A 84 403–7
[22] Wang S and Magnusson R 1993 Appl. Opt. 32 2606