Fs-laser processing of polydimethylsiloxane

Petar A. Atanasov, Nikolay N. Nedyalkov, Eugenia I. Valova, Zhenya S. Georgieva, Stefan A. Armyanov, Konstantin N. Kolev, Salvatore Amoruso, Xuan Wang, Ricardo Bruzzese, Miroslaw Sawczak, and Gerard Śliwiński

---

Fs-laser processing of polydimethylsiloxane

Petar A. Atanasov,[1,a)] Nikolay N. Nedyalkov,[1] Eugenia I. Valova,[2] Zhenya S. Georgieva,[2] Stefan A. Armyanov,[2] Konstantin N. Kolev,[2] Salvatore Amoruso,[3] Xuan Wang,[3] Ricardo Bruzzese,[3] Miroslaw Sawczak,[4] and Gerard Śliwiński[4]

[1]*Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Shose, Sofia 1784, Bulgaria*
[2]*Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 11, Sofia 1113, Bulgaria*
[3]*CNR-SPIN, Dipartimento di Scienze Fisiche, Universita degli Studi di Napoli Federico II, Complesso Universitario di Monte S. Angelo, Via Cintia, I-80126 Napoli, Italia*
[4]*Photophysics Department, The Szewalski Institute, Polish Academy of Sciences, 14 Fiszera St, 80-231 Gdańsk, Poland*

We present an experimental analysis on surface structuring of polydimethylsiloxane films with UV (263 nm) femtosecond laser pulses, in air. Laser processed areas are analyzed by optical microscopy, SEM, and μ-Raman spectroscopy. The laser-treated sample shows the formation of a randomly nano-structured surface morphology. μ-Raman spectra, carried out at both 514 and 785 nm excitation wavelengths, prior and after laser treatment allow evidencing the changes in the sample structure. The influence of the laser fluence on the surface morphology is studied. Finally, successful electro-less metallization of the laser-processed sample is achieved, even after several months from the laser-treatment contrary to previous observation with nanosecond pulses. Our findings address the effectiveness of fs-laser treatment and chemical metallization of polydimethylsiloxane films with perspective technological interest in micro-fabrication devices for MEMS and nano-electromechanical systems. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4887812]

I. INTRODUCTION

Polydimethylsiloxane (PDMS) is an important technical polymer and has various uses in medical or industrial fields, thanks to its many outstanding characteristics. It belongs to the group of polymeric materials called silicones, possessing the common characteristic of a backbone composed by an alternate succession of Si and O atoms joined together via strong, covalent inter-atomic bonds. The Si atoms couple to two adjacent O atoms and two organic radicals, i.e., C-H or C-R, where R is an organic group. The various silicones only differ from each other by these organic radicals, e.g., methyl (-CH), vinyl (-HC=CH), hydrocarbure, or other organic functional groups. Silicone rubbers also fall in this class of materials, but usually include some additives as fillers, plasticizers, and cross-linkers. Silicones have high molecular weight ($\geq 5 \times 10^5$ g/mol), exhibit very low electrical conductivity, and are transparent to visible (VIS) and infra-red (IR) light usually absorbing below 280 nm (i.e., above 4.4 eV). Due to their chemical inertness, silicones are perfect biocompatible materials and are widely used as medical implants.

Chemical coupling of foreign species to silicone requires to open its structure, which involves an irreversible modification and inter-atomic bond breaking.[1,2] However, this may not be done by a mechanical way. Thermal means are also inappropriate since silicone does not melt, sublimate, or evaporate, but transforms into a glassy and extremely fragile material at temperatures exceeding 230 °C.

PDMS is a flexible elastomer that makes it an excellent material for micro-fabrication of MEMS devices.[3] One useful property of PDMS is that its surface can be chemically modified in order to obtain interfacial properties of interest.[4] For example, PDMS can be covalently functionalized through exposure to a reactive oxygen plasma, whereby surface Si-CH$_3$ groups transform into Si-OH groups. These silanol surfaces are easily transformed with alkoxysilanes yielding a much different chemistry.[5,6]

The use of laser radiation offers a useful approach to the processing and selective surface functionalization of silicone. In particular, UV nanosecond laser pulses (e.g., KrF, ArF, and F$_2$) are largely applied for fabrication of optical elements,[7–9] deposition of thin films,[10–12] modification of optical properties,[13–15] and surface processing or functionalization.[16–22] For example, KrF excimer laser ($\lambda = 248$ nm) processing of siloxane-based flexible silicone rubber is used to photo-decompose the sample surface changing the surface relief.[2,22–24] Information on the changes to the PDMS structures irradiated by ns-laser pulses is typically obtained by μ-Raman measurements.[22] Laser irradiation can obviously induce cracking of the chemical bonds, but it can also be used in the ablation regime to micro- or nano-structure the polymer surface, thus enhancing adhesion of a metal film.[23,24]

Recently, laser processing with femtosecond (fs) pulses is gaining increasing interest and micro-fabrication of PDMS polymer with IR fs pulses is investigated in some studies.[25–28] For example, Huang and Guo studied fs laser ablation of PDMS induced by 900 fs, 1552 nm laser pulses both on a fixed spot and for continuous line formation.[25] They observed a threshold fluence of ≈ 4.6 J/cm^2, and analyzed the

a)Author to whom correspondence should be addressed. Electronic mail: paatanas@ie.bas.bg.

influence of pulse overlap rate and irradiation energy on line width, internal ablation interface depth, and ablation surface quality. Many of the investigations exploiting fs laser pulses are restricted to IR wavelengths, and studies concerning UV fs ablation of PDMS are still scarce.

Here, we report experimental results on UV (263 nm) fs-laser structuring of PDMS films deposited on glass or Si substrates. The processed areas are analyzed by optical and SEM microscopies and μ-Raman spectroscopy. Moreover, we also report the possibility of chemical metallization by Pt or Ni of the laser-processed areas. Finally, we discuss some practical aspects of laser treatment and metallization of the processed areas with respect to use such a complex method for micro-fabrication of a PDMS device in MEMS.

II. EXPERIMENTAL

A chirped-pulse-amplification Nd:glass laser system delivering $\approx$300 fs pulses at 527 nm, obtained by second-harmonic-pulse compression of the fundamental output (i.e., 1055 nm, $\approx$0.9 ps), at a repetition rate of 33 Hz, was used in the experiments. UV pulses of $\approx$300 fs duration at 263 nm were generated by second harmonic generation in a KD*P crystal. The laser beam is focused on the sample to a laser spot of $\approx$2.8 $\times$ 10^{-4} cm^2 by using a lens with 250 mm focal length. In all experiments, the energy per pulse is varied between 80 and 180 μJ by using neutral density filters, the corresponding energy density (fluence) varies in the range of 0.3–0.65 J/cm^2. The PDMS sample is mounted on a rotating stage moving with at a constant speed of 2 or 5 rotations per minute. During experiments, the laser beam is also moved in one direction by a scanning mirror, thus obtaining a circular processed area on the sample, with up to $\frac{1}{2}$ of the laser spot width overlapping of the laser points and up to 2 subsequent laser pulses on one point.

Silicone sheets (Statice Sante MED 4860, 4870, or 4880) with a thickness of 0.25 mm are deposited on different substrates: glass or Si. This specific silicone is polydimethyl-siloxane (PDMS) filled with different quantities of silica foam (nanodispersed SiO$_2$). The optical absorption of the material at 263 nm is measured to be $\sim$12%.

The processed areas are viewed by optical microscope and analyzed by SEM. μ-Raman scattering analyses at both 514 and 785 nm excitation wavelengths are carried out, and the results are rationalized according to the detailed study on PDMS reported in Ref. 29. The beam spot on a sample for both wavelengths is $\sim$5 $\times$ 5 μm^2 for 100$\times$ objective, which is smaller enough than the processed area in the laser spot. The tight-focusing of the microscope limits the effective column from which the signal is effectively recorded. Moreover, the ablation depth achieved is several μm and fs-laser pulses could, namely, affect a short depth, close to the surface. Having in mind all this aspects, we consider that the comparison between μ-Raman spectra of native and processed material is adequate and the effect of the non processed material in depth if any is minor.

Advanced electro-less metallization technique is developed and it is applied for metallization, by Pt or Ni, of the laser-processed area by using hydrazine hydrate as reducing
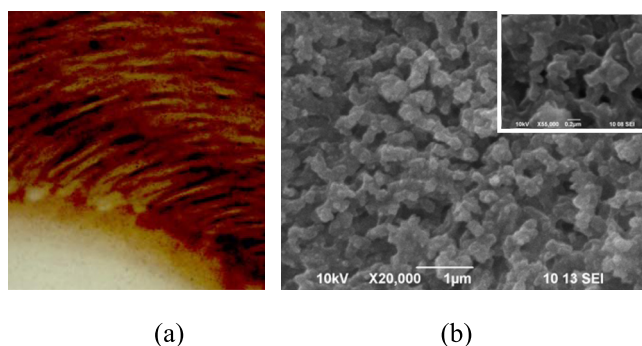

FIG. 1. (a) Optical image of a part of the processed PDMS area. (b) SEM micrograph of the fs laser-processed PDMS film. The inset in panel (b) reports an enlarged view of the processed area illustrating the nanostructured morphology of the processed PDMS surface. Laser energy is 176 μJ per pulse (0.65 J/cm^2).

agent. The pH of the plating baths is $\sim$12, and the deposition temperatures are 70 °C for Pt and 80 °C for Ni, respectively. The deposition is performed for 25 min in a thermo stated vessel, under rigorous stirring. Metallization of the laser-processed PDMS samples is successfully achieved. The details of metallization procedure will be described in a forthcoming communication.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows an optical image (a) and a SEM micrograph (b) of a part of the PDMS sample processed at a fluence of 0.63 J/cm^2. It is evident that ablation depth is higher in the inner part of the processed circular area, where the overlapping of the subsequent laser pulses is higher. SEM picture in Fig. 1(b) evidenced that the sample surface presents a nanostructured morphology. The inset in Fig. 1(b) shows a SEM micrograph at higher magnification, illustrating the random arrangement of the sub-micron structures and the presence of some voids.

μ-Raman spectroscopy of the processed samples at two excitation wavelengths, namely, 514 nm (VIS light) and 785 nm (IR light), is carried out. Prior to the Raman analyses, spectra of native PDMS sample are registered, and typical signals are reported in Fig. 2. Both spectra show similar
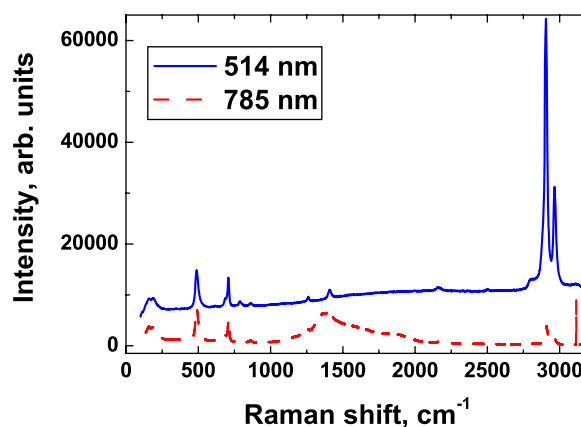

FIG. 2. μ-Raman spectra of the native PDMS-elastomer registered at two different excitation wavelengths: 514 nm (VIS light) and 785 nm (IR light). The signals are vertically shifted to facilitate the readability of the data.
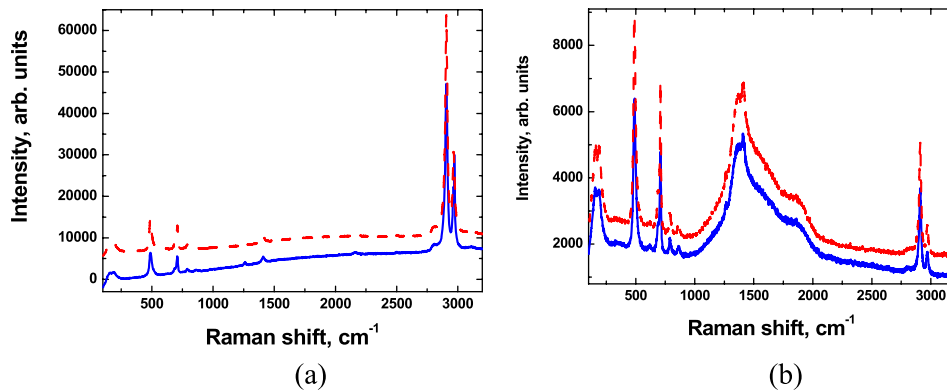
FIG. 3. Raman spectra of PDMS after fs laser-treatments at a fluence of 0.65 J/cm^2 for two different excitation wavelengths: (a) 514 nm; (b) 785 nm. The corresponding spectra of the native PDMS-elastomer processed. Dashed lines—native material; solid lines—laser processed material.

structures, the different intensities of the Raman peaks being due to the different excitation wavelengths. To facilitate the readability of the data, in Fig. 2, the signals are vertical shifted. For a Raman shift up to ∼1000 cm^{-1}, a similar peak intensity is observed in both spectra. At longer Raman shift, a strong and broad feature is discerned between 1250 and 1450 cm^{-1} for IR excitation, with three peaks at 1266, 1370, and 1409 cm^{-1}, respectively. All these peaks can be assigned to the methyl vibrations.[29] For VIS excitation, the peaks at 1266 and 1406 cm^{-1} have quite low intensity. Furthermore, the peaks of the stretching methyl group at 2907 and 2965 cm^{-1} are very strong in case of VIS excitation. This, in turn, suggests that VIS excitation is preferable to follow the methyl stretching group.

Fig. 3 reports the μ-Raman spectra of the laser-processed PDMS at VIS (a) and IR (b) excitation wavelengths and compares them with those of the native sample. It is clear that the characteristic features of μ-Raman spectra of the laser-treated sample are quite similar to those of the native PDMS-elastomer. However, the intensities of the various peaks show some differences. All characteristic peaks of the PDMS-elastomer (i.e., symmetric stretching vibrations of Si-O-Si at 488 cm^{-1}; Si-C symmetric stretching at 708 cm^{-1}; Si-CH$_3$ rocking vibrations at 678, 787, and 862 cm^{-1}; stretching vibration of the methyl group at 2907 and 2907 cm^{-1}; and methyl bending vibrations at 1266 and 1409 cm^{-1} as well as 1370 cm^{-1}) show a reduction of the signal intensity after laser treatment.

Our results do not show any evidence of elementary silicon formation induced by laser treatment, contrary to what is observed earlier in Refs. 21 and 22, when UV, ns-laser pulses are used. Moreover, peak shift is observed for ns-laser

treatment. Such an effect is absent for UV, fs pulses as exemplified in Fig. 4, which reports a closer comparison of the Raman peaks corresponding to Si-O-Si and Si-C vibrations (panel a) and CH$_3$ vibrations (panel b), registered for the native and the laser-treated samples at a fluence is 0.65 J/cm^2 and with excitation at 785 nm. A similar behavior occurs for the excitation at 514 nm.

We also analyzed the effects of the laser fluence on the Raman peaks. Figure 5 summarizes the experimental observation by reporting the intensity variation of the different peaks: Si-O-Si stretching vibrations at 488 cm^{-1} (circles), Si-C symmetric stretching at 708 cm^{-1} (squares), CH$_3$ symmetric stretching at 2907 cm^{-1} (triangles), and asymmetric stretching at 2965 cm^{-1} (open triangles). One can observe that the intensity of the Raman peaks corresponding to each mode linearly decreases with the raise of the laser fluence. The effect of laser fluence is stronger in case of Si-O-Si stretching vibrations at 488 cm^{-1} and Si-C symmetric stretching at 708 cm^{-1}. The decrease of the vibrational lines intensity caused by laser treatment is a measure of irreversible degradation or breaking of some inter-atomic bonds and formation of the free open radicals.

After laser treatment, electro-less metallization, by Pt or Ni, of the laser-processed PDMS samples is successfully carried out. Figure 6 shows an optical image of the metallized surface, which suggests UV, fs laser-treatment as a promising tool for a two-step processing of PDMS surface metallization. It is important to mention here that the time interval between laser processing and electroless deposition is not critical in this case, contrary to earlier experimental observations on PDMS laser processing with nanosecond pulses.[21] In fact, metallization is also accomplished after several
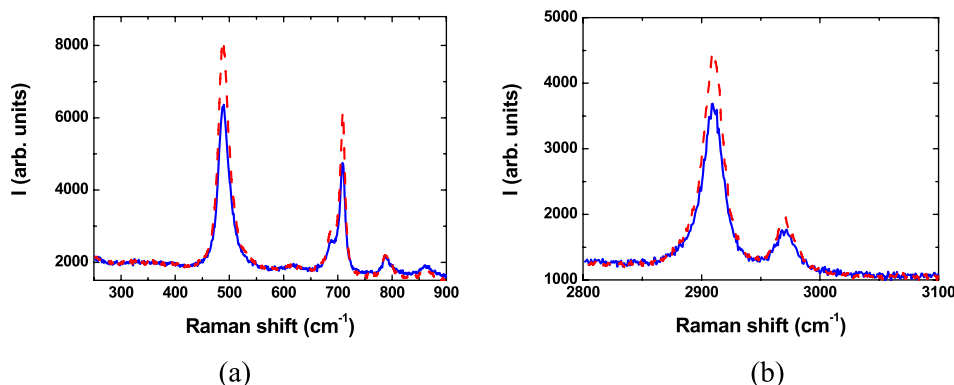

FIG. 4. Raman peaks using excitation at 785 nm corresponding to (a) Si-O-Si and Si-C vibrations and (b) CH$_3$ vibrations, after laser treatment. Dashed line—native material; solid line—laser processed material. The fluence is 0.65 J/cm^2.
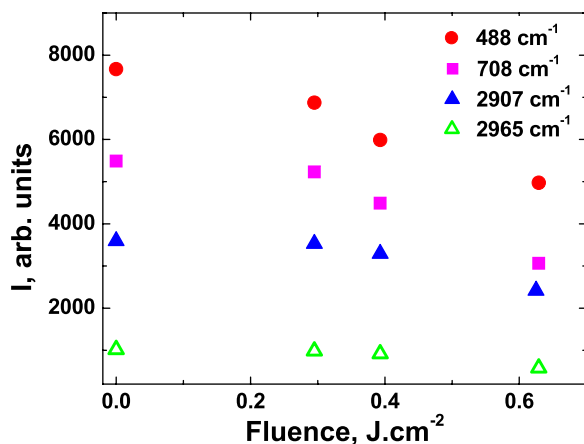
FIG. 5. Dependence of the intensities of the peaks corresponding to Si-O-Si stretching vibrations at $488 \, cm^{-1}$ (circles), Si-C symmetric stretching at $708 \, cm^{-1}$ (squares), CH_3 symmetric stretching at $2907 \, cm^{-1}$ (triangles) and asymmetric stretching at $2965 \, cm^{-1}$ (open triangles) on the energy density of laser processing.

FIG. 6. Optical microscope image of a part of the metallized tracks.

months from the laser-treatment. We believe that this can be ascribed to both the nano-structuring of the material surface and/or effective breaking of Si-O-Si, Si-C, and CH_3 bonds.

IV. CONCLUSION

In summary, we have investigated UV fs laser surface processing of polydimethylsiloxane films deposited on different substrates, in air. The laser-treated sample surface becomes very rough with nanosize random structures. The intensities of the Si-O-Si stretching mode at $488 \, cm^{-1}$, Si-C symmetric stretching at $708 \, cm^{-1}$, and CH_3 symmetric stretching at $2907 \, cm^{-1}$ strongly decrease with the increase of the laser fluence. Advanced electro-less technology is developed and successful metallization with Pt or Ni of laser processed traces is accomplished. The metallization does not depend on the time interval between laser-treatment and electro-less plating. This is ascribed to the nano-structuring of the surface and/or effective breaking of the atomic bonds of the material, indicating UV, fs laser-treatment as a

promising tool for a two-step process of PDMS surface metallization.

[1]K. W. Kolasinski, "Lasers in surface science," Curr. Opin. Solid State Mater. Sci. **13**, 1 (2009).
[2]L. Laude, A. Rowley, M. Humayun, and J. Weiland, "Nanoscale surface activation of silicone via laser processing," U.S. patent: 2008/10305320 A1 (2008).
[3]J. C. McDonald, D. C. Duffy, J. R. Anderson, D. T. Chiu, H. Wu, O. J. Schueller, and G. M. Whitesides, Electrophoresis **21**(1), 27 (2000).
[4]H. Makamba, J. H. Kim, K. Lim, N. Park, and J. H. Hahn, Electrophoresis **24**(21), 3607–3619 (2003).
[5]Brochure of the Company Gelest, *Silicon Compounds: Silanes and Silicones* (Gelest, Inc., Morrisville, PA, 2004), p. 560.
[6]G. T. Hermanson, A. K. Mallia, and P. K. Smith, *Immobilized Affinity Ligand Techniques* (Academic Press, San Diego, CA, 1992), p. 454.
[7]M. Okoshi, J. Li, and P. R. Herman, Opt. Lett. **30**, 2730 (2005).
[8]H. Takao, H. Miyagami, M. Okoshi, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **44**, 1808 (2005).
[9]H. Takao, M. Okoshi, H. Miyagami, and N. Inoue, IEEE J. Sel. Top. Quantum Electron. **10**, 1426 (2004).
[10]H. Takao, M. Okoshi, and N. Inoue, Appl. Phys. A **79**, 1567 (2004).
[11]M. Okoshi, M. Kuramatsu, and N. Inoue, Appl. Surf. Sci. **197–198**, 772 (2002).
[12]M. Okoshi, M. Kuramatsu, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **41**, 1395 (2002).
[13]M. Okoshi, M. Iyono, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **48**, 122503 (2009).
[14]M. Okoshi, M. Iyono, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **48**, 102301 (2009).
[15]M. Okoshi, D. Sekine, N. Inoue, and T. Yamashita, Jpn. J. Appl. Phys., Part 2 **46**, L356 (2007).
[16]M. Okoshi, M. Iyono, N. Inoue, and T. Yamashita, Appl. Surf. Sci. **255**, 9796 (2009).
[17]M. Okoshi, J. Cho, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **46**, 1516 (2007).
[18]H. Takao, M. Okoshi, and N. Inoue, Appl. Phys. A **79**, 1571 (2004).
[19]M. Okoshi, T. Kimura, H. Takao, N. Inoue, and T. Yamashita, Jpn. J. Appl. Phys., Part 1 **43**, 3438 (2004).
[20]H. Takao, M. Okoshi, and N. Inoue, Jpn. J. Appl. Phys., Part 2 **41**, L1088 (2002).
[21]C. Dupas-Bruzek, O. Robbe, A. Addad, S. Turrell, and D. Derozier, Appl. Surf. Sci. **255**, 8715 (2009).
[22]C. Dicara, T. Robert, K. Kolev, C. Dupas-Bruzek, and L. D. Laude, Proc. SPIE **5147**, 255 (2003).
[23]J. W. Dini, Met. Finish. **95**, 10 (1997).
[24]L. D. Laude, "Process for metallization of plastic materials and products thereto obtained," U.S. patent 5,599,592 (1997).
[25]H. Huang and Z. Guo, J. Micromech. Microeng. **19**(5), 055007 (2009).
[26]H. Huang and Z. Guo, Lasers Med. Sci. **25**(4), 517 (2010).
[27]H. Huang, "Polymer and tissue separation and micro/nano-fabrication via ultra-short pulsed laser plasma-mediated ablation," Ph.D. thesis (The State University of New Jersey, 2010).
[28]Y. Fukami, M. Okoshi, and N. Inoue, Jpn. J. Appl. Phys., Part 1 **43**, 4240 (2004).
[29]S. C. Bae, H. Lee, Zh. Lin, and S. Granick, Langmuir **21**, 5685 (2005).