Optical Processing

5

Micro-lens Array Assisted Nano-Patterning on Stainless Steel using Picosecond Laser

Sunita Kedia*[1, 4], **Pratiksha Pawar**[2], **Kiran Yadav**[2], **A. K. Sahu**[3] **and J. Padma Nilaya**[1,4]

[1]Laser & Plasma Technology Division, Bhabha Atomic Research Centre, Trombay – 400085, INDIA
[2]Department of Physics, K. J. Somaiya, Vidyavihar, Mumbai – 400077, INDIA
[3]Glass & Advanced Material Division, Bhabha Atomic Research Centre, Trombay – 400085, INDIA
[4]Homi Bhabha National Institute, Training School Complex, Anushaktinagar, Mumbai – 400094, INDIA


Various patterns generated on SS sample

ABSTRACT

Optical near-field processing by employing contact particle lens array leading to effective nano-patterning on metal surface using a picosecond pulsed laser has been demonstrated. The technique utilizes self-assembled monolayer of polystyrene colloidal microspheres as near-field optical confinement structure on 316L stainless steel (SS). Each microsphere, acting as a micro-lens, focuses the incident laser beam leading to material ablation and pit formation underneath. The characteristics of pitting depend sensitively on the laser parameters, particle and substrate material properties. These nano features may have diverse applications including inscribing security features.

KEYWORDS: *Micro-lens, Nano-patterning, Picosecond laser, Monolayer, Colloidal particles*

Introduction

Nano-patterning on surfaces have wide ranging applications in diverse areas, e.g., biosensors, display, data storage, solar cells, security etc. [1-5]. Designing unique nanoscale patterns on metal surfaces with limits on its replication can provide a high level of security against fraudulent activities [6]. Generation of nano-patterns on metals and semiconductors usually employ costly, multi-step and time-consuming lithography processes which limit production throughputs [7,8]. In last decade or so, particle lens array has evolved as one of the near field techniques for laser-based surface nano-patterning on substrates [8] and has gained popularity as a contactless process with ability to generate surface features smaller than the diffraction limit. In this process, a hexagonally close packed monolayer of spherical colloidal particles is deposited on a smooth surface by self-assembly method. When exposed to a laser pulse of appropriate fluence, each particle acts as a micro-lens and focuses the incident laser beam at particle-substrate contact point where the beam intensity enhances to a level as to cause ablation of substrate material resulting in the formation of nano-pits [9,10]. Depending upon the laser spot size, wavelength, intensity and the substrate and particulate materials, nano-patterns can be generated on polymer surfaces [11], hydrophobic surface [8], semiconductor substrates [12] etc. In the absence of any particulate absorption, it is understandable that higher is the laser intensity, larger would be pit dimensions. Needless to say, the substrate properties, e.g, its absorption at the incident wavelength, melting point etc. also play an important role in this process.

We present here, our experimental results of nano-patterning on 316L stainless steel alloy (SS) surface by means of polystyrene (PS) colloidal particle (dia ~2.3 μm) monolayer irradiated by a single pulse from a picosecond laser operating at 532nm. A focused laser beam with a sub-mm spot size was allowed to shine upon the mono layer of particles. Coupled with computer controlled linear translation stage, patterns well discernable by eye were generated on the substrate surface with each point in the pattern holding a sub-pattern of nano-pits. The size, depth, and density of the nano-pits could be sensitively regulated by controlling the laser power, laser wavelength and diameter of colloidal particles respectively. If characterized thoroughly, this technique can be gainfully employed as a security feature that can be inscribed on any surface which may be a part of an important instrument that requires protection from replication. Apart from standardizing methods to generate monolayer of particles on substrates over large areas, nano-pits of diameter ranging from ~0.5 μm to 1.5 μm on SS substrates by varying laser energy from 0.3 mJ to 2.5 mJ respectively, have been generated as sub-structures of main patterns on SS substrate. The pattern 'BARC' on SS sample with and without monolayer was compared where the single direct laser pulse irradiation yields a single spot of size ~100 μm whereas, monolayer assisted irradiation leads to the creation of ~ 2000 nano-pits within the same area.

Materials and Methods

A novel method for the generation of monolayer on SS substrate was conceived and Fig.1(a) shows the sequence of steps followed. Commercially procured aqueous colloidal solution of monodispersed PS microsphere (M/s. Spherotech Inc.) of diameter ~2.3 μm and 5% w/v concentration was appropriately diluted in ethanol and subsequently ultrasonicated for 20 min. The colloidal mixture was drop-cast on water surface in a Petridish where the PS particles floated on the surface of the liquid (density of PS (0.0005 g /cm³) was less than methanol (0.79 g /cm³) and water (1 g /cm³)). The dilution was optimized such that the particles formed monolayer on water surface. Mirror polished SS substrates (diameter: 2 cm) with average roughness of ~1.5 nm were cleaned with methanol. Monolayer of PS settled on water

---

**Author for Correspondence: Sunita Kedia*
E-mail: skedia@barc.gov.in

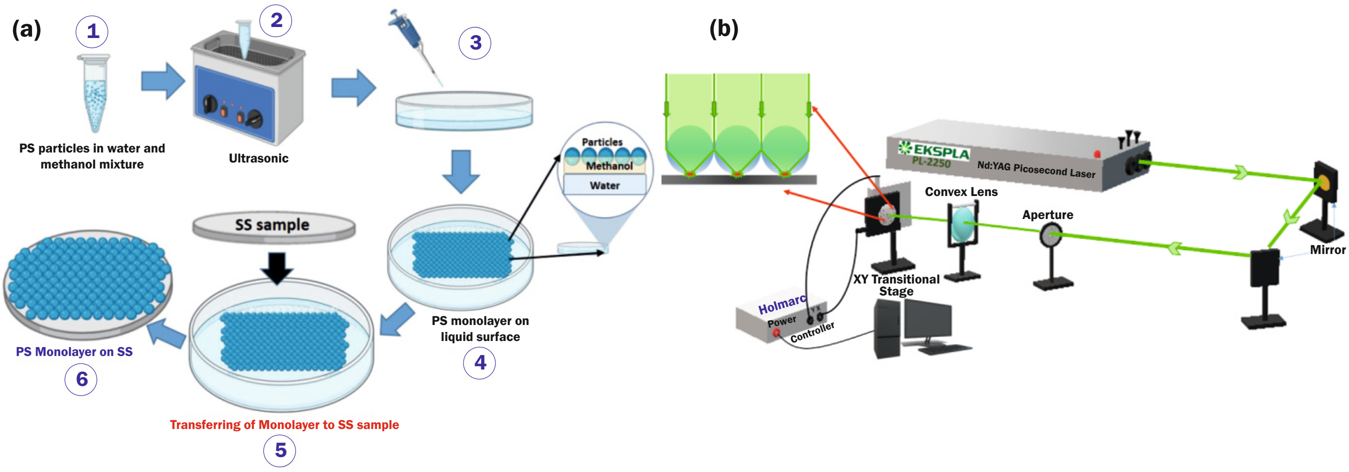

Fig.1: (a) Pictorial depiction of PS monolayer preparation on SS substrate (b) Experimental set up for laser assisted pitting, inset: simple rendition of focusing of the incident laser beam through micro particles.

surface was carefully transferred to the SS and was allowed to dry in ambient with adequate protection from dust. Deposition of PS monolayer was confirmed using scanning electron microscope (SEM) images. An Nd:YAG picosecond pulsed laser (M/s. Ekspla; PL2250) with pulse duration ~30 ps emitting at 532 nm was used to irradiate the PS monolayer. The substrate surface was exposed to a single laser pulse that was steered and focused (10 cm focal length lens) on to the sample. The laser beam affected spot diameter was ~100 μm and contained ~2000 microparticles. Under ideal conditions of irradiation, each PS particle can give rise to a pit (inset of Fig.2(b)) and therefore, a sub-pattern of ~2000 nano-pits can be generated in one laser spot.

The analytic expression for microsphere induced pitting for sphere radius $r >> \lambda$ is given by N. Arnold as follows [13].

$$w = r\sqrt{\frac{(4-n^2)^3}{27n^4}} \qquad (1)$$

where n is the refractive index of the sphere and λ is wavelength of incident light. As per equation-1, the laser spot size on the substrate will increase with particle size.

To be noted that, depending upon the spatial variation of laser intensity as a result of focusing, characteristics of pits generated under one laser shot may not be identical. However, this can be avoided by managing uniform intensity of the incident beam. Distance between two laser shots was maintained as 350 μm and various patterns were generated on the sample using computer controlled X-Y stage. The residues of the PS particles were removed post laser irradiation by immersing the sample in toluene for ~5 min. For sake of comparison, pattern of 'BARC' was generated on SS sample with and without monolayer, keeping all other parameters constant and the difference between then in the micro-nano scale is evaluated.

Results and Discussion

Fig. 2(a) shows the SEM images of PS monolayer on SS sample where hexagonally closed packed monolayer of PS particles can be seen in the inset of the figure. Fig.2(b) is a photograph of the sample where monolayer covering large surface area (~3 cm^2) of SS can be seen, the variation in surface color is an artifact due to reflection off the PS particulates. Fig.2(c) and its inset are the SEM image of the sample surface irradiated by single laser pulse (30ps, 1mJ) and subsequently cleaned in toluene showing nano-pits in closed packed arrangement on the substrate surface. Fig.2(d) shows the photograph of a sample, with residual particulates post irradiation, on which 'BARC-DAE' has been inscribed. Some other patterns were tried with the same experimental set-up, photographs of which after removing the monolayer in toluene are shown in Fig.2(e).

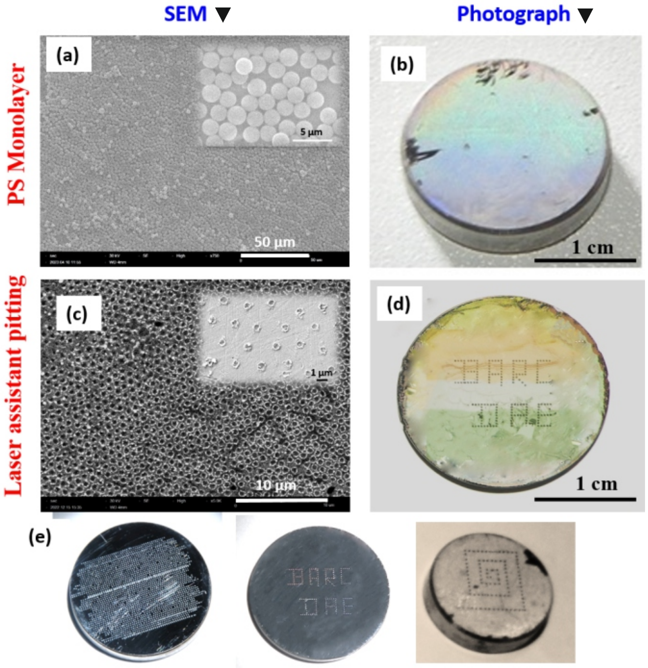

Fig.2: (a) SEM image and (b) photograph, of PS monolayer on SS sample. (c) SEM image and (d) photograph, of laser assisted pitting on SS sample and (e) various pattern generated on SS sample.

Fig.3(a) and 3(b) are photograph of SS samples on which 'BARC' pattern has been created without and with PS monolayer, respectively. While both images appear similar to the eye, they are significantly different in micro-nano scale. A single beam of focused laser pulse on a substrate surface devoid of particulates results in a laser affected region (extending over ~100 μm) comprising of melted and resolidified portion at the centre surrounded by heat affected zone that depends on the spatial profile of the focused laser beam. Further magnification of this region shows undulations of the surface, a signature of the process mentioned above. The dark spots visible on the surface of sample (marked with arrows) are inherent defects on SS. However, in case of particle deposited surface, the focusing effect causes ablation and

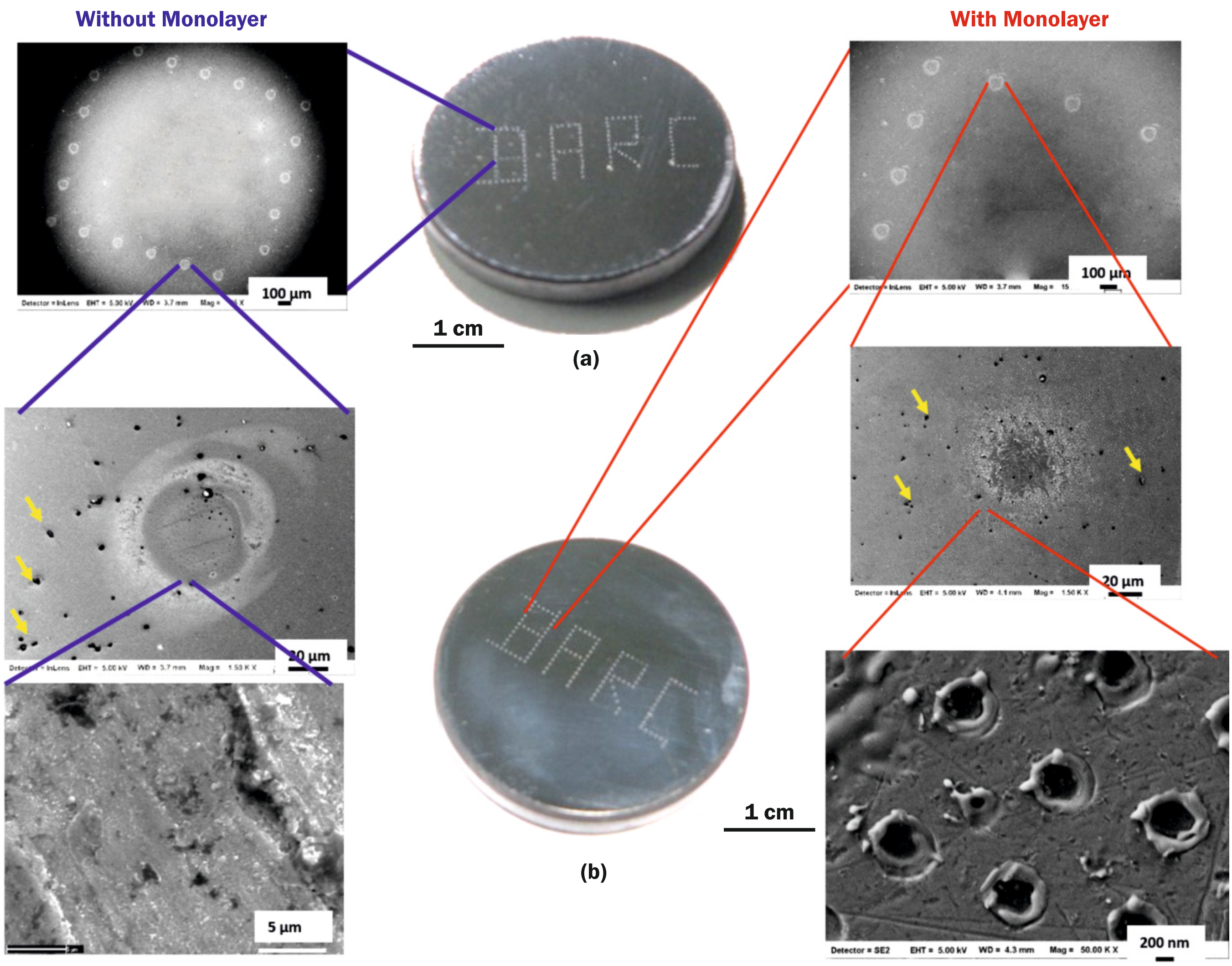

Fig.3: Photograph, SEM image at different magnification of pattern generated on SS sample (a) without PS monolayer and (b) with PS monolayer.

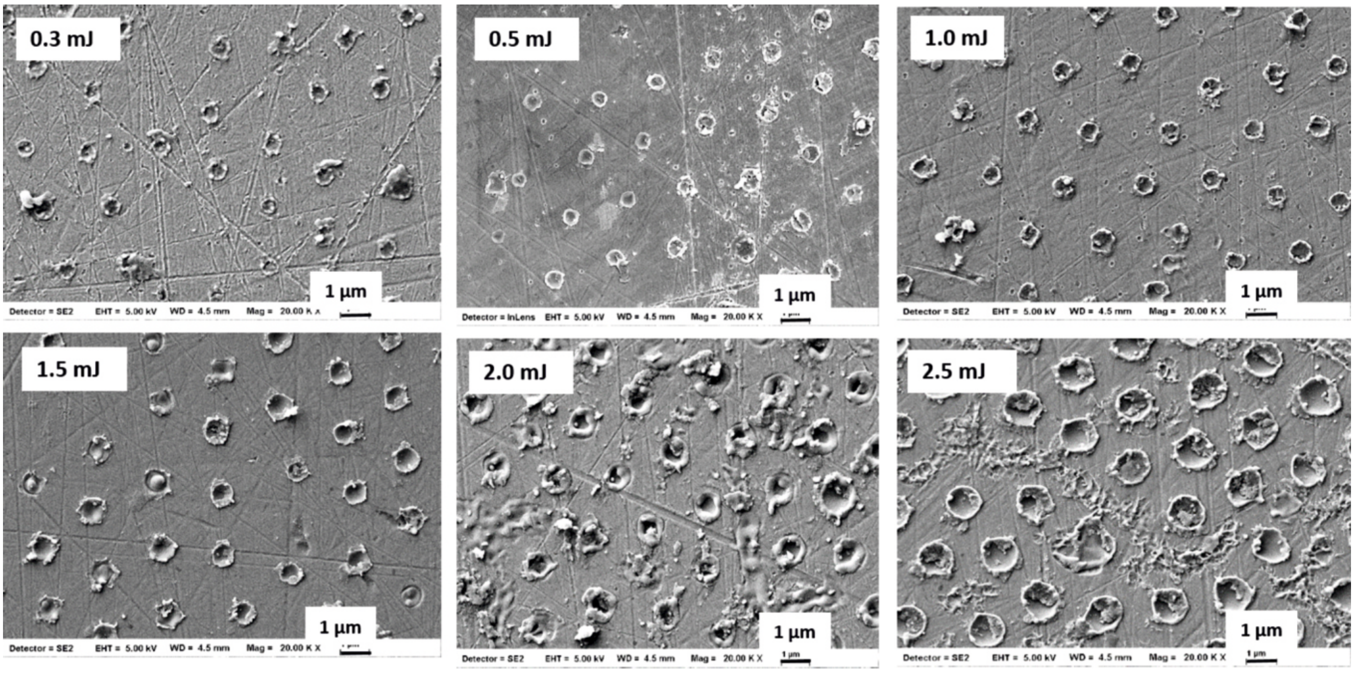

Fig.4: FE-SEM images of the pits generated on SS sample at different incident laser energy.

formation of pits and the same laser affected region has ~2000 nano-pits of diameter ~500 nm in it, as can be seen in the magnified (50 KX, scale bar- 200 nm) SEM image of Fig.3(b). Dimension, depth and separation between these nano-pits can be controlled and manipulated by varying laser power, pulse duration, wavelength, and diameter of micro-particles. As an example, Fig.4 shows the change in pit dimension with variation in laser energy.

The SEM images of pits generated at various laser energy per pulse on SS surface using PS monolayer of particle size ~2.3 μm. An increase in pit diameter from 0.5 μm (at 0.3 mJ) to 1.5 μm (at 2.5 mJ) is clearly visible in the images. This is due to an increase in the laser intensity at the contact point of particle and surface with increased laser power that in turn increases the area where ablation occurs.

Further investigations for a thorough parametric characterisation of this technique such as, depth profile vis-à-vis laser parameters, effect of microsphere diameter, surface oxidation, effect on mechanical properties of the surface, reproducibility, use of different materials such as polymers, and scaling-up are being planned.

Conclusions

In conclusion, we have demonstrated a simple method of surface nano-patterning by particle assisted pulsed laser irradiation that can be scaled up easily. The characteristics of the nano-pits can be altered in a controllable manner by changing the laser parameters and the dimension of the particles. The technique of contact particle lens array assisted surface patterning appears promising, apart from other applications, in inscribing nano-security features on surfaces.

Acknowledgements

The authors gratefully acknowledge constant support and guidance of Head, Laser & Plasma Technology Division and of Group Director, Beam Technology Development Group. They also acknowledge Nayna Jadhav, IRLS, BARC for technical help.

References

[1] V. Naresh and N. Lee, A review on biosensor and recent development of nanostructured materials enabled biosensors, Sensor 21 (2021) 1190.

[2] Z. Chai, A. Childress and A. A. Busnaina, Direct assembly of nanomaterials for making nanoscale devices and structure: Mechanisms and applications, ACS Nano 16 (2022) 17641.

[3] J. Yu, M. Luo, Z. Lv. S. Huang, H. H. Hsu, C. C. Kuo, S. T. Han and Y. Zhou, Recent advantages in optics and optoelectronic data storage based on luminescent nanomaterials, Nanoscale 12 (2020) 23391.

[4] S. M. Lee, R. Biswas, W. Li, D. Kang, L. Chan, and J. Yoon, Printable nanostructured silicon solar cells for high-performance, large-area flexible photovoltaics, ACS Nano 8 (2014) 10507.

[5] J. Rajendran, R. Karri, J. B. Wendt, M. Potkonjak, N. McDonald, G. S. Rose, and B. Wysocki, Nano meets security: exploring nanoelectronics devices for security applications, Proceedings of the IEEE, 103 (2015) 829.

[6] J. Kim, J. M. Yun, J. Jung, H. Song, J. B. Kim and H. Lhee, Anti-counterfeit nanoscale fingerprints based on randomly distributed nanowires, Nanotechnology 25 (2014) 155303.

[7] Y. Xia and G. M. Whitesides, Soft Lithography, 28 (1998) 153

[8] A. Khan, Z. Wang, M. A. Sheikh, D. J. Whitehead and L. Li, Laser micro/nano patterning of hydrophobic surface by contact particle lens array, Applied Surface Science 258 (2011) 774.

[9] B. Sugathan, J. P. Nilaya, V. P. M. Pillai, and D. J. Biswas, Particle assisted structuring on metallic substrate: Anomaly when particle size exceeds irradiation wavelength, AIP Advanced 10 (2020) 035222.

[10] X. Sedao, T. Jy. Derrien, G. W. Romer and B. Pathiraj, Laser surface micro-/nano-structuring by a simple transportable micro-sphere lens array, Journal of Applied Physics 112 (2012) 103111.

[11] C. Farcau and S. Astilean, Simple colloidal lithography approach to generate inexpensive stamps for polymer nano-patterning, Materials Letters 65 (2011) 2190.

[12] B. Sugathan, J. P. Nilaya, V. P. M. Pillai and D. J. Biswas, Observation of particle assisted nano-ring, bump, pit structures on semiconductor substrate by dry laser exposure, AIP Advanced, 8 (2018) 115110.

[13] N. Arnold, Theoretical description of dry laser cleaning, Appl. Surf. Sci. 208 (2003) 15.