Laser processing for strengthening of the self-restoring metal-elastomer interface on a silicone sheet

Kiyokazu Yasuda
Dept. of Materials, Physics, & Energy Engineering, Nagoya University,
Furo-Cho, Chikusa, Nagoya, Aichi 464-8603, Japan
E-mail: yasuda@numse.nagoya-u.ac.jp

Abstract. A self-restoring microsystem is a unique concept which realizes the sensing functionality and robust interface which mechanically and electrically connects a deformable object such as a human body with printed electronic devices. For this purpose, the formation of conductive wiring on an elastomer substrate was attempted using the nickel ink printing process. Before the wiring process, surface patterning of a silicone sheet by a galvano-scanned infrared laser was conducted for the enhancement of interface adhesion of the metal deposit and polymer. Characterization of the fabricated pattern was conducted by optical microscopy. The novel method was successfully demonstrated as a fabrication of selective patterns of metal particles on self-restoring MEMS.

1. Introduction

With the progress in the field of nursing care as well as the advanced medical and engineering fields, the measurement of biological signals have been actively employed for the man-machine interface, brain-machine interface, and myoelectric hand [1-6]. Meanwhile, the developments of sensors and accurate measurements are needed without any restrictions. The sensors detect temperature, blood flow pulsating sound pressure, electromyography (EMG), heart telegraph signal, and brain wave which occur due to human activity. Since they are small and have weak signals with variations, the measurement requires high accuracy and sensitivity [7, 8]. As the technology requires such signal measurements to be achieved, it is important to consider the structure composed of new eco-friendly and bio-compatible materials and their interfaces for connecting electronic devices to a flexible human body electronically and mechanically [9,10].

In this paper, the fine structure of the device such as a thermistor is considered as a temperature sensor on a polymeric silicone elastomer material which is a promising bio-material interface. Such flexible polymer base devices are stretchable (typically several tens of percent deformation in length) and they can recover to their initial shape according to the human body motion because of their elastic and surface attaching nature, namely known as self-restoring characteristics. However, the circuit pattern printing on a hydrophobic surface such as silicone is one of the problems for creating stable patterns. Figure 1 shows the line patterns that became discontinued to isolated droplets after printing.

In order to solve such a problem, the effect of fine irregularities of the surface texturing treatment to the polymer substrate by a CO₂ laser was investigated. In addition, the influence of the contact angle of pure water as an indicator of the printed wiring conductor formed subsequently on the substrate was investigated. Finally, a trial to print a selection of the dipping in the solution after the pattern of dispersed nickel particles to the surface by the CO₂ laser was conducted.
2. Experimental
In the experiment, a silicone polymer (Nitto Denko, #66, thickness: 0.5 mm) was cut to a length of 25 mm as a sheet substrate. A micro-focused scanning CO$_2$ laser system (Keyence ML-9110, max. output power: 12 W, wavelength: 10.6 $\mu$m) was used for the surface pretreatment of the polymer sheet substrate as shown in figure 2.

As for the irradiation area (10 mm $\times$ 8 mm) by a CO$_2$ laser marker, 100 columns by 56 rows of micro lines (width: 150 $\mu$m) were drawn repeatedly. The irradiation time was 30 s. The laser output was varied from 120 mW to 720 mW for the surface treatment. In order to maintain the planarity, the substrate was fixed on a flat slide glass and a laser beam was focused on the polymer surface. The patterned surface of the substrate was observed by optical microscopy and FE-SEM. The contact angle of a distilled water droplet on the irradiated surface was measured to examine the wettability and consequently, the relevant index of adhesiveness of post-formed conductive pattern prints. The silicone sheet was used as the substrate material since it is considered to have the closest biocompatibility to human activities among the rubber polymer materials. The physical properties of the silicone elastomer sheet are shown in Table 1. A solution of nickel particles (Mitsui Mining & Smelting Co., Ltd, average diameter: 15 nm) in deionized water was prepared as the printing material.

![Figure 1](image1.png)  
**Figure 1.** Hydrophobic property of a silicone sheet.

![Figure 2](image2.png)  
**Figure 2.** Surface modification of a silicone sheet by a scanning CO$_2$ laser.

| Physical properties of a silicone sheet. |
|-----------------------------------------|
| **Tensile strength (MPa)** | **Elongation (%)** | **Adhesion force (N/19mm)** |
| 8.2 | 660 | 39 |
| **Resistivity (Ω cm)** | **Contact angle (water)** |
| 2.8 x 10$^{15}$ | 105 |
3. Results and discussion

The typical surface texture after the laser irradiation of line patterns is shown in figure 3. The laser irradiation power was varied from 120 mW to 720 mW. The line pattern was drawn in the area of 10 mm x 8 mm. According to the optical microscopic observation, no apparent modification of the surface state was observed in the case of a low laser output power of below 240 mW. With the increase of the laser output above 360 mW, the area turned into a white mass on the surface of silicone. Fiber-like structures were also identified along with the formation of a fine white stripe texture line for the CO\textsubscript{2} laser irradiation area. In the case of over 600 mW, the debris (white area) was deposited along the irradiated area. As the irradiated power was increased, the silicone surface was significantly altered and exhibited fine structures. This fine structure was considered to be fabricated due to the thermal decomposition of the smooth surface of the silicone polymer to nanoparticles as debris. The periodical pattern of the surface was found to be deformable even after severe elongation of the sheet which might be suitable for a bio-interface since self-restoring property was required.

Figure 3. Optical image of the silicone surface after scanning CO\textsubscript{2} laser patterning.
Figure 4 is SEM microphotographs of the laser irradiated area. From this observation, it is clear that the irradiated area on the surface had a disordered microstructure with particulates and small grooves. The temperature increase by CO$_2$ laser irradiation was estimated over the melting point of silicone. This fact indicated that the origin of the particulates-like mounds was the melting mass of silicone. They seemed to evolve from the original sheet surface and adhere firmly. Since the temperature change was very abrupt, the volume shrinkage during cooling caused open grooves on the surface. Moreover, in the magnified photo of figure 4(b), a fibrous structure in the nanometer scale on the rough surface in the micrometer scale was observed. All those changes of the surface topography greatly cause the increase of the net area of the silicone surface after the laser irradiation. It can be emphasized that this hierarchical structure was easily produced by only the thermal laser treatment which enabled the formation of arbitrary patterns.

Figure 5 is the measurement result of the contact angle of deionized water droplets on the laser-irradiated region of the sheet material. There was no significant change in the surface wetting characteristics in the case of laser power less than 240 mW. The values of contact angle were almost the same level as the initial condition before the laser irradiation. The silicone rubber used in this experiment has a thermal stability up to approximately 523 K. From the fact that there was no change in both the morphology and wetting characteristics, it is clear that the surface retains its initial chemical composition as polymeric silicone. For the case of the medium laser power, especially at 360 mW, the variations in contact angle values were detected which infer the instability of the surface condition. As shown in figure 4, the local surface properties should be different between the white line area and non-irradiated area. The wettability measured by means of the contact angle of water droplets larger than these line pattern pitches reflects the instability of the measured contact angles.

The values of the contact angle in the cases of 480 mW and 600 mW were approximately 20°-30° larger than those of the original silicone rubber which had high water repellency (contact angle: 110°). This slight increase suggests that the periodic deep 3D structures of line patterns enhance water repellency. In contrast, greater wetting with small contact angles of 16°-40° was observed due to high hydrophilicity in the case of the high laser power condition of 720 mW. The steep change of wetting property is believed to result from structural changes in the surface texture by increasing laser power as well as the formation of a reaction substance having a hydrophilic group on the top surface by the thermal decomposition generated during the laser irradiation.
Figure 5. Laser power vs. contact angle of water.

(a) Array pattern by laser  (b) Magnification of (a)

(c) Deposition of nickel particles  (d) Magnification of (c)

Figure 6. Nickel particles printing on the silicone polymer sheet after laser patterning.
After the modification process by CO\textsubscript{2} laser irradiation, the printing of nickel particles was conducted. Figure 6 showed nickel printing images observed under the optical microscope on the silicone polymer sheet. Before printing, the silicone polymer was irradiated by the CO\textsubscript{2} laser so that an array dot pattern (300 \( \mu \text{m} \) in diameter) formed. The laser treated silicone was immersed in the water solution of nickel particles. As shown in figures 6(c) and (d), the nickel particles were printed only on the surface area except on the array dot area where the laser was focused. The top surface of the laser irradiated dot area tightly attracts water molecules which might prevent nickel adhesion, while nickel particles reside on the other area, although water molecule can escape by a repulsive force due to surface high hydrophobic property. It was concluded that the selective printing was achieved by only the arbitrary template patterning by laser irradiation and post simple immersion in a liquid solution of metal particles.

4. Conclusions

By increasing the output of CO\textsubscript{2} laser irradiation on the surface of the silicone rubber, different texture structures on the surface were observed. In particular, very high hydrophilicity property appeared in the case of an output power of 720 mW. Using a scanning CO\textsubscript{2} laser process, the self-restoring silicone sheet exhibited hydrophobic (\( \geq 100^\circ \)) property at the medium laser power condition, while showing a steep transition to exhibiting hydrophilic (16\(^\circ\)-40\(^\circ\)) property at the high laser power condition. The abrupt change of surface property from hydrophobic to hydrophilic coincides with the morphology change from the periodic regular structure to the disordered structure with the increase of the laser intensity. It is suggested that the flexible silicone polymer sheet is selectively printable by the simple immersion of the nickel particle solution using the prior scanning CO\textsubscript{2} laser irradiation. The proposed laser process is considered to be applicable to such self-restoring polymeric sheet devices where the interface between the metal and polymer should be strengthened.

References

[1] Birbaumer N 2006 Psychophysiology \textbf{43} 517
[2] Wolpaw J R 2002 \textit{Clinical Neurophysiology} \textbf{113} 767
[3] Santhanam G, Ryu S I, Yu B M, Afshar A and Shenoy K V 2006 \textit{Nature} \textbf{442} 195
[4] Ganguly K, Dimitrov D F, Wallis J D and Carmena J M 2011 \textit{Nat. Neurosci.} \textbf{14} 662
[5] Chin T 2010 \textit{Jpn. J. Rehabil. Med.} \textbf{47} 33
[6] Parker P, Englehart K and Hudgings B 2006 \textit{J. Electromyography and Kinesiology} \textbf{16} 541
[7] Hattori T, Sato T, Minato K, Nakamura H and Yoshida M 2008 \textit{Trans. Jpn. Soc. Med. Biol. Eng.} \textbf{46} 268
[8] Ito D, Ozeki M, Nakamura Y, Sakurazawa S, Toda M and Akita J 2008 \textit{Human interface} \textbf{10} 107
[9] Sekido N, Yasuda K and Takai O 2011 \textit{Proc. 17th Symp.Microjoining Assembly Technol. in Electronics} \textbf{257}
[10] Yasuda K, Sekido N and Takai O 2011 \textit{Proc. Int. Conf. Electronics Packaging (ICEP)} 2011 981