

Journal of Materials Science and Applied Energy



Journal home page: jmsae.snru.ac.th

The Deposition Times of Teflon Thin Films by PECVD Technique Affecting to Peel-off of PDMS Molding in Micro-Nano Structure for Surface Enhanced Raman Spectroscopy

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Received 8 June 2020; Revised 23 June 2020; Accepted 21 September 2020; Available online: 1 January 2021

Abstract

In this research, we have studied the thickness of Polytetrafluoroethylene (PTFE) or Teflon thin films layer on Nano-in-Micro structure scale by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. Especially, the deposition time are various at 5-20 min and tested manually Teflon peeling-off from PDMS template for SERs applications. After tested peeling-off, a magnetron sputtering system is used to decorate the PDMS molding with silver nanoparticles for 180 s. The PDMS template was investigated by Field-emission Scanning Electron Microscopy (FE-SEM) and Raman Spectroscopy. The PDMS template was observed the hydrophobic properties by contact angle measurement. The result indicated that the thickness of the Teflon film layer related with the number of peeling-off from the PDMS template which can be observed from the intensity of Raman signal by testing with Rhodamine 6G (R6G) concentration of 1×10^{-5} M. FE-SEM result showed the thickness of Teflon films was increased from 50.78-210.37 nm. in accordance with deposition time. The contact angle indicated that Teflon can easily help to peel-off PDMS template than un-coating. The optimum deposit time is 20 min and can peel-off of PDMS template into 5 cycles that can be observed by Raman intensity is remaining stable.

Keywords: Teflon; PECVD Technique; PDMS Molding; SERs applications

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Introduction

The development for chemical and biosensing applications that can bind together with molecular fingerprint particularity potential single-molecule sensitivity [1 - 5] is Surface Enhanced Raman spectroscopy (SERs). The analyze molecules on the SERs substrate by "hot

spots" plasmonic is strongly enhanced local electromagnetic fields induced by the excitation of the collective oscillation of free electrons in noble metals [6]. The most regular substrates used for the growth of SERS active layers are silicon wafers and glass slides. However, disadvantages of these substrates are rigid and brittle and heavily limit the applications of plasmonic effect. The traditional brittle and rigid substrates have disadvantages over flexible substrates because of their ability to correspond to the various objects, can be coiled onto curved surfaces and can be simply cut into different shapes and sizes. For examples, they can be desire for non-planar, flexible or conformal surfaces. Presently, the conventional polymer substrate which is nontoxic, chemical stable, mechanically flexible and can encounter the demand of flexibility is Polydimethylsiloxane (PDMS) which has been widely used in bendable applications [7 - 9]. However, Polytetrafluoroethylene (PTFE or Teflon) is similarity applications with PDMS but prominent point is nonreactive, partly because of the strength of carbon-fluorine bonds in applications containers and pipework for reactive and corrosive chemicals resistance. It is hydrophobic which can increasingly amplify the Raman signal to reach more sensitive detection and high heat resistance. PTFE or Teflon commonly is used as a non-attach coating especially in pans and other kitchenware. In the past, more research was prepared SERs on silicon substrate which has high production costs. Therefore, we try to reduce costs by developing SERs substrate on Aluminum (Al) sheet and made PDMS template on Al sheet that is quite rough and difficult to prepare in nano to micrometer scale.

In this research is focus on to reduce cost by coated Teflon layer on the PDMS template. The tested the number of the peel-off of PDMS template from Aluminum sheet was studied. The optimum deposition time of the Teflon layer which can be tested with Rhodamine 6G (R6G) concentration of 1×10^{-5} M. from the intensity of Raman signal. The PDMS template was observed the hydrophobic properties by contact angle measurement. We tried to improve PDMS surface to hydrophobic properties because if the surface is hydrophobic, PDMS peel-off cannot be damage and examined the morphology and measured the Teflon thickness that was affect PDMS template peeling performance by using Field Emission Scanning Electron Microscopy (FE-SEM).

Materials and Methods

The preparation of the aluminum sheet with size of 4×4 cm² and thickness of 0.04 mm was used as a pattern for the PDMS molding. Laser marking to engrave in the preparation the surface to make the pattern on aluminum sheet in nano to microstructure scale with fixed power 12 W, speed 300 mm s⁻¹, fill space 0.02 mm and area size of engraving is 5×5 mm² [10, 11]. The scrubbed aluminum sheet with detergent to remove the dirt and grease stains after that dried with nitrogen is the first cleaning process. The coating of Teflon thin film layers on aluminum sheets surface was applied with Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. The deposit Teflon thin film layers by various deposition times at 5, 10, 15, and 20 min, respectively, with released Tetrafluoroethylene gas (C_2F_4) was investigated. The mixing PDMS and curing agent at 10:1 ratio is the preparation of PDMS molding process and then released the bubbles from this process by desiccator for 1 h in a vacuum oven. The PDMS molding was again degassed for 1 h and annealed at 75 C° for 3 h and obtained the PDMS template. Sputtering technique with magnetron sputtering system is the tool for decoration of silver nanoparticles which prepared on the PDMS templates. The sputtering condition process was operated at 3×10^{-3} mbar under

9 sccm of Argon gas flow, current 0.10 A and deposition time of 180 s by using silver target (99.99 % purity). The efficiency of Teflon peel-off was studied by the intensity of Raman signal model RENISHAW in Via plus Raman system and tested the number of PDMS molding peel-off until it was torn from the template. The morphology and measured the thickness thin films with Field Emission Scanning Electron Microscopy (FE-SEM) was studied.

Results and Discussion

Morphology of Aluminum Sheet by Laser Marking

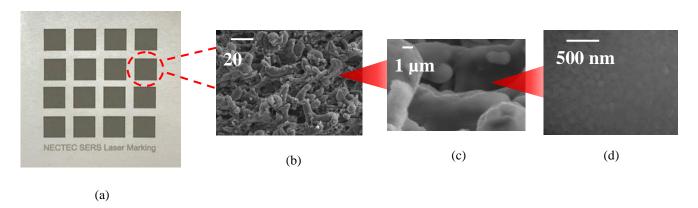


Fig. 1 FE-SEM images of aluminum sheet by laser marking.

The morphology of Aluminum sheet in Nano-in-Microstructure by using laser marking to engrave in the preparation the surface template was studied to make a PDMS template according to Aluminum sheet pattern. Fig. 1 (a) – (d) show the magnification of laser marking template scale from 20 μm – 500 nm, respectively. The roughness of the surface of Aluminum sheet pattern is rather uniform that can help the PDMS adhesion with Aluminum substrate.

The Characteristic of the Peeling-off PDMS Molding from Template

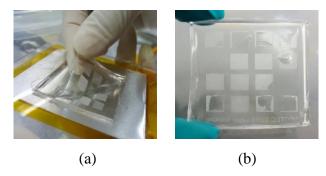


Fig. 2 (a) Peel-off of PDMS molding and (b) The tear characteristic of the peeling-off PDMS molding from template.

Figure 2 (a) shows PDMS template that was difficult to peel-off from the Aluminum sheet and Fig. 2 (b) displays the surface of the PDMS template that was torn without coated Teflon. Fig. 2 shows that if prepared the engraved aluminum sheet without Teflon coating on template, it was

hard to peel-off PDMS and made tore of PDMS surface. Therefore, the study of the Teflon layer coating can help to peel-off the PDMS with a complete Aluminum patterned as the prototype.

The Study of the Thickness of the Teflon at Various Times from 5-20 min By a Field Emission Scanning Electron Microscope (FE-SEM)

Figure 3 (a) shows Teflon thickness results by using FE-SEM, checks the Teflon thickness from FE-SEM images that obtained from the coating of Teflon thin film on silicon substrate. From FE-SEM, the thickness of Teflon deposition at 5, 10, 15 and 20 min are 50.78, 129.53, 151.45 and 210.37 nm, respectively. It can be seen that, when the deposition times increased, the film thickness should increase accordingly which was consistent with the principles.

PDMS template after peel-off of PDMS molding shows in Fig. 3 (b), it can be seen that the Teflon coated on aluminum sheet pattern effect to peeling-off of PDMS molding is easy and zoom in this area presents the complete PDMS surface by without tearing.

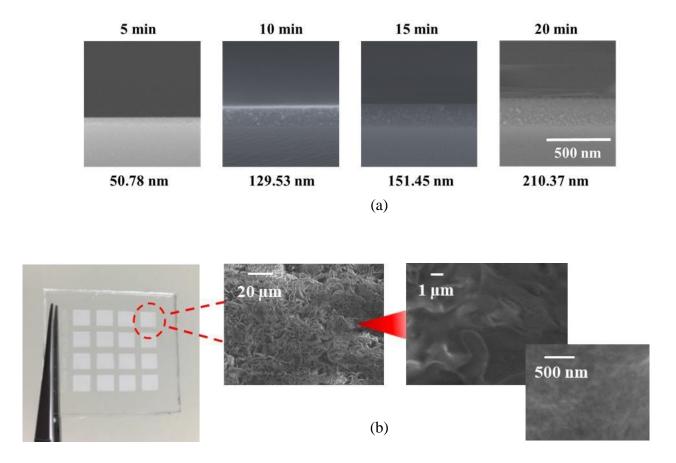


Fig. 3 (a) FE-SEM images of the Teflon thin film on silicon substrate and (b) FE-SEM images of the PDMS template after peel-off of PDMS molding with Teflon thin film.

The Hydrophobic Properties from Contact Angle Measurement

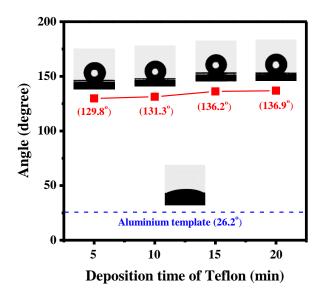


Fig. 4 Contact angle measurement of Teflon by varying deposition time.

Figure 4 shows that the contact angle is increased with enhancing the Teflon decoration time from 129.80° – 136.90° when compared with Aluminum substrate which the contact angle is 26.20°. This result supported the superhydrophobic properties when Teflon deposition time increased. The Teflon coating could help to increase the hydrophobic properties of the substrate [12] and resulting in more time able to easily the peel-off the PDMS template. The contact angle measurement is used to analyze the hydrophobic properties of SERS. The superhydrophobic surface is greatly supportive for strong enhancement of the Raman signal [13, 14].

Raman Intensity Test PDMS Template by Using Raman Spectroscopy Technique

In this step, the PDMS template of the peel-off cycle 1-5 will be applied to all deposition times of the Teflon thin film to test the intensity of Raman signal of Rhodamine 6G (R6G) at concentration of 1×10^{-5} M. The results show that the feature of the peaks can be clearly identified at the location 1300, 1360 and 1505 cm⁻¹, respectively that are the C-C bond, as shown in the Fig. 5.

By controlling the deposition times of Teflon onto aluminum sheet at 5-15 min after peeling-off the PDMS template at Fig. 5 (a) - (c) shows the intensity of the Raman signal will gradually decrease as the number of peel-off cycles increases. It can be clearly seen that at the 5th cycle of 5-15 min deposition times presents rarely R6G Raman signal. Contrary to the coating of Teflon thin film on the aluminum sheet for 20 min with peel-off cycle 1-5, the intensity of R6G Raman signal is approximately the same as shown in Fig. 5(d). Therefore, it can be seen that the conditions for coating Teflon thin film onto the aluminum sheet mold from the deposition time is 20 min that able to peel-off template many times and is still highly effective in amplifying Raman signals.

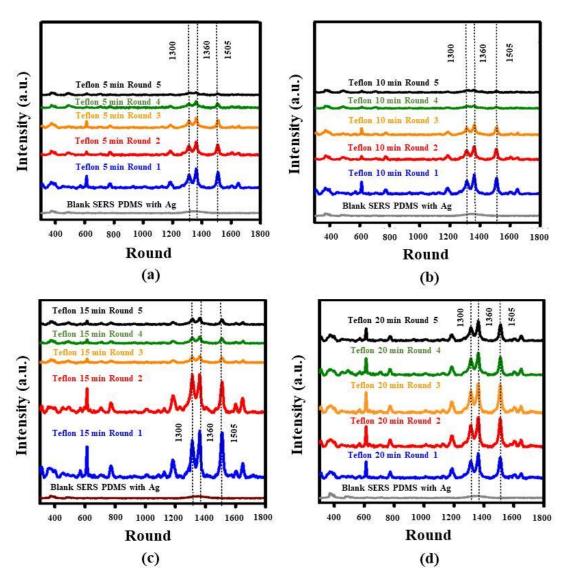


Fig. 5 Raman intensity of PDMS template of the peel-off cycle 1-5 in all deposition times of the Teflon.

The relationship of between the average Raman peak signal and the number of the peel-off cycle of PDMS template

In considering the Raman result by selecting the R6G main peak from Fig. 5 of 1300, 1360 and 1505 cm⁻¹ was calculated to average Raman intensity in each round. Figure 6 shows a black point line on the top is the Teflon deposition in 20 min that is more straight line than other color point lines that means the Raman signal is remaining stable although the number of the PDMS template peel-off rounds was increased to 5 cycle. The result displays that the best conditions for deposition Teflon thin films on aluminum sheet time is 20 min.

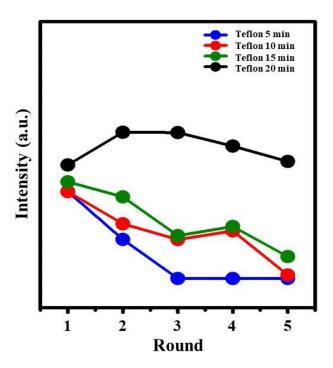


Fig. 6 Relationship between the average Raman peak signal and the number of the peel-off cycle of PDMS template.

Conclusion

In this experiment was introduced PDMS template on Aluminum sheet to replace silicon substrate that is high cost in Surface Enhanced Raman Spectroscopy applications. The control of the deposition time for coating Teflon thin film on aluminum sheet by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique was studied. Teflon thin film coating PECVD technique enhances the hydrophobic properties of the aluminum sheet in nanometer to micrometer scale on aluminum sheet, a highly rough surface. This makes it easy to peel the PDMS template by without torn and can be peeling-off into 5 cycles and tested the intensity of Raman signal with R6G is remain stable. From contact angle result was supported that Teflon used as a non-stick coating and shows the super-hydrophobic properties. The best condition for Teflon film coating is deposition time at 20 min and thickness is 210.37 nm.

Acknowledgement

Thanks to department of Industrial Physics and Medical Instrumentation (IMI) of King Mongkut's University of Technology North Bangkok and Optical Thin-Film Technology Laboratory (OTL), National Electronics and Computer Technology Center (NECTEC), Pathumthani, Thailand. This research was funded by Faculty of Applied Sciences at budget in 2020, King Mongkut's University of Technology North Bangkok, contract no. 6343102.

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