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Flexible surface-enhanced Raman spectroscopy sensor for wearable devices

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Summary:

We report the fabrication and characterization of a flexible, nanostructured surface-enhanced Raman spectroscopy sensor designed for integration in wearable optical devices. This sensor utilizes the biocompatible material FlexDym®, which offers excellent flexibility and advantages in manufacturing. The nanostructures are embossed through a temperature and pressure-assisted molding process using a silicon master. The fabricated SERS structures exhibit significant enhancement in Raman signal detection. This work advances state-of-the-art in flexible SERS and wearables.

Keywords: SERS, wearable sensors, biosensors, nanofabrication, Raman spectroscopy

Background

Raman spectroscopy provides a molecular fingerprint signal that corresponds to the specific structural vibrations of molecules, enabling label-free detection. Surface-enhanced Raman Spectroscopy (SERS) amplifies the Raman signal by 10^{10} to 10^{11}-fold using nanostructured metallic surfaces, thereby achieving very high sensitivity [1]. Recently, flexible SERS has garnered significant interest due to its potential in a wide range of applications, particularly for detecting molecules on irregularly shaped objects [2]. These applications include non-invasive detection of biomarkers in biological tissues, food safety monitoring for pesticides and contaminants in fruits, vegetables, and other food items, textile analysis for dyes and chemicals on fabrics, forensic science for trace detection of drugs and explosives on various surfaces, and environmental monitoring. FlexDym® used in this work is the first prototyping material specifically designed for microfluidics community as an alternative to PDMS, offering flexibility, mouldability, scalability, transparency and resistance to molecules adsorption. It also has been shown to have no harmful effects to the human body when in contact for a prolong amount of time (ISO certified for interaction with blood, in vitro cytotoxicity, systemic toxicity, etc. [3]). To leverage these advantages, we developed a novel fabrication process for flexible SERS sensors using FlexDym®.

Methods

The nanostructured masters for molding SERS (various periodic patterns with characteristic dimensions in the range of 170–330nm, and depth 200-600nm) were fabricated in a cleanroom using a combination of UV-Nanoimprint Lithography (UV-NIL) and Dry Reactive Ion Etching (DRIE) [4] (Fig. 1 A-D). For the molding process, FlexDym® sheets are placed over the Si masters, with controlled temperature and pressure conditions using a portable embossing setup. This ensures the accurate transfer of nanostructures from the Si master to the FlexDym® sheets. The molded FlexDym® sheets are then separated from the master, resulting in flexible SERS substrates with the desired nanostructures. The final step involves coating the FlexDym® substrates with a layer of gold (60 nm) using a sputter tool (Q150R ES, Quorum Technologies, UK) (Fig.1 E-H). This gold coating enhances the SERS effect by providing the necessary metallic surface for signal amplification.

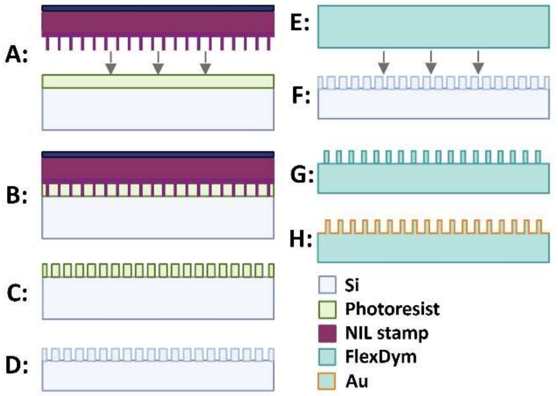

Fig. 1. A simplified schematic of the fabrication flow of a mold in Si (A to D) and the flexible SERS device (E to H).

The fabricated sensor consists of 4 active SERS areas 1mmx1mm each, with periodic, rectangular nanostructures, coated with 60nm Au (Fig 2).

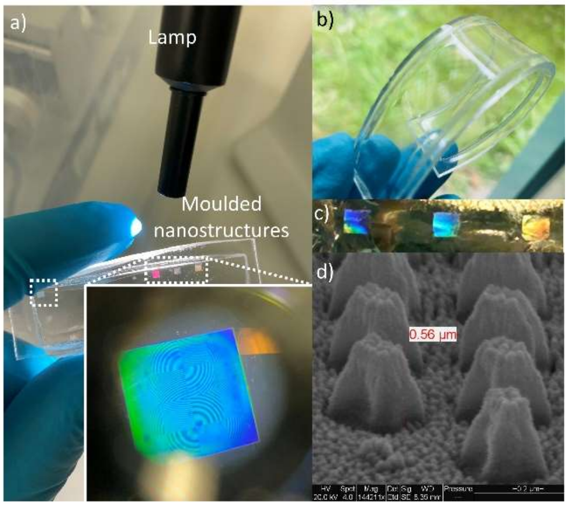

Fig. 2.a) A photograph of molded substrate with four SERS areas 1mm x 1mm each, and an optical microscopy image of the molded SERS in FlexDym® showing characteristic diffraction pattern; b) A photograph of; c) Molded SERS coated with 60nm of gold; d) SEM of the metasurface master used for molding.

Results

For the SERS measurements a BWS465-785S i-Raman Plus spectrometer with a fiber probe and 785nm excitation wavelength was used. Rhodamine 6G (R6G, Merck KGaA) which was diluted in water and used as a sample for benchmarking and comparison with other published works. 6 µL of R6G was pipet onto SERS chips and left to dry. The measured Raman intensity shows excellent enhancement of the fabricated nanostructures and a different level of enhancement depending on the nanostructures shape (Fig. 3a). To evaluate the performance of the flexible SERS sensors, three different FlexDym® material thicknesses were tested: 250, 750, and 1200 µm. The Raman spectra obtained from different thicknesses showed similar SERS responses, indicating that the thickness of the FlexDym® material does not affect the enhancement of the Raman signal (Fig. 3b).

Conclusions

We presented a flexible SERS sensor fabricated using novel and biocompatible material FlexDym®. The nanostructured SERS chips are molded and replicated, allowing for efficient fabrication with high accuracy possible for mass production. Moreover, the approach allows for a straightforward integration with other Si- or glass-based components and supports innovations requiring molding of ultra-small structures. Future work will include combining the SERS sensor with flexible microfluidic chip with a submicroliter chamber with inlets for passive sample collection.

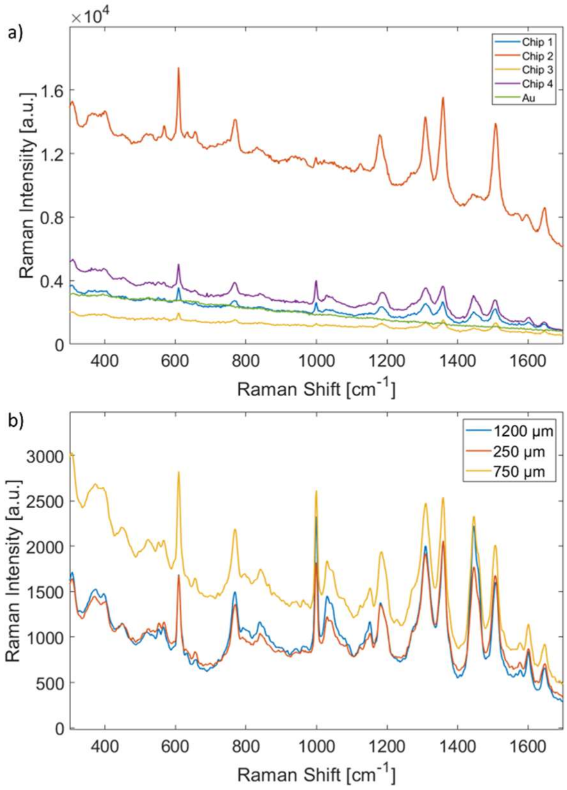

Fig. 3. Measured Raman spectra of a) 1mM R6G dried on 250µm FlexDym® SERS and on gold for comparison; b) R6G on SERS in molded in three thicknesses 250, 750 and 1200µm of FlexDym® material.

References

[1] E.C. Le Ru et al. Enhancement Factors: A Central Concept during 50 Years of Surface-Enhanced Raman Spectroscopy, ACS Nano 18(14), 9773-9783 (2024); doi:10.1021/acsnano.4c01474

[2] K. Xu et al., Toward Flexible Surface-Enhanced Raman Scattering (SERS) Sensors for Point-of-Care Diagnostics. Adv. Sci. 6, 1900925 (2019); doi:10.1002/advs.201900925

[3] https://eden-microfluidics.com/flexdym-microfluidic-chips/

[4] C.A. Dirdal et al. UV-Nanoimprint and Deep Reactive Ion Etching of High Efficiency Silicon Metalenses: High Throughput at Low Cost with Excellent Resolution and Repeatability, *Nanomaterials* 13, 3 (2023); doi:10.3390/nano13030436

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