

Highly Sensitive Surface-enhanced Raman Spectroscopy Sensors by 3-D Nanoimprint Lithography

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We have reported highly sensitive surface-enhanced Raman Spectroscopy (SERS) sensors of Au deposited on Si nanograss fabricated by RIE etching using a Bosch process.^{1,2} Those sensors achieved an enhancement factors of 6×10^7 for trans-1,2-bis(4-pyridyl)-ethylene (BPE) molecule.^{1,2} However, there are some issues for Si nanograss based systems: the substrate is an expensive single crystal and the silicon can absorb both incident and scattered light, making it difficult to improve the performance further and investigate the SERS enhancement mechanism. To address these issues, we developed a process to replace the Si nanograss by a cross-linked polymer nanograss fabricated by 3-D nanoimprint lithography (NIL)³. This technology produced SERS sensors with enhancement factors about 10 times better than that of Si nanograss. Moreover, we demonstrated that NIL is a great tool to pattern high-resolution 3-D nanostructures and opened a door of fabrication and integration of high sensitive SERS sensors based on 3-D nanostructures.

NIL duplicates 3-D information into the resist material instead of just 2-D information like most other lithographic techniques, and therefore it is an ideal tool to fabricate complex 3-D structures, such as nanograss. First, a polymer daughter mold⁴ on a glass substrate was created by nanoimprinting Si nanograss patterns into a 2 μm thick UV-curable NIL resist. The pattern in this daughter mold was the reversed nanograss configuration. Then, the daughter mold was used in another NIL process to re-create the nanograss pattern in a layer of UV-cured NIL resist. Figure 1a shows the original Si nanograss mold, and Fig. 1b shows the polymer nanograss replica. Sharp tips with radius about 10 nm were successfully duplicated. Finally, 80 nm of Au was deposited onto both the nanograss substrates by electron-beam evaporation to complete the SERS sensor fabrication. (fig. 1c) Figure 2a compares Raman spectra of BPE at 785 nm excitation obtained using the best Si nanograss sensor, a polymer nanograss sensor, which was duplicated from that Si nanograss, on a glass substrate, a polymer nanograss sensor imprinted on top of metal mirror, and a nanoimprinted “reversed” nanograss sensor. Nanoimprinted nanograss samples demonstrated performance improvements of factors of 3 and 5 respectively. Moreover, we achieved another factor of 3 improvement by using a polymer nanograss with a height taller than that optimized for Si nanograss. (fig. 2b)

¹ M. Hu, J. Tang, F. S. Ou, H. P. Kuo, S. Y. Wang, Z. Li, and R. S. Williams, *Proceeding of SPIE* **7312**, 731201 (2009).

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⁴ H. X. Ge, W. Wu, Z. Y. Li, G. Y. Jung, D. Olynick, Y. F. Chen, J. A. Liddle, S. Y. Wang, and R. S. Williams, *Nano Letters* **5**, 179 (2005).

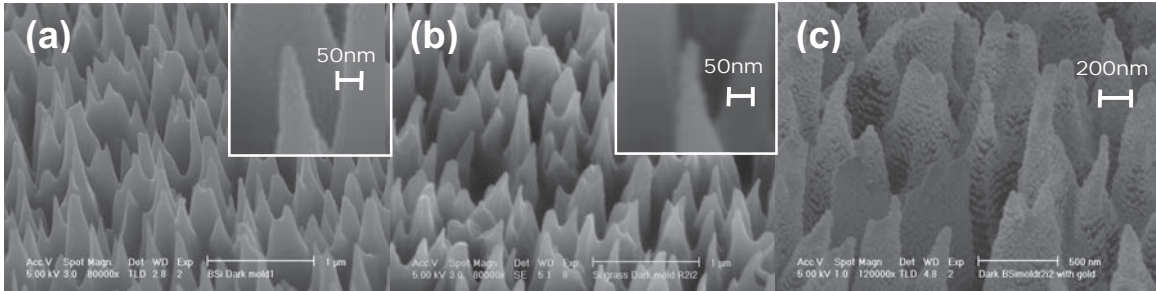


Fig. 1 (a) SEM images of a Si nanogras substrate. (b) SEM images of nanogras duplicated in nanoimprint resist by 3-D NIL. (c) SEM image of a nanogras substrate with Au nano-particles deposited. Sharp tips in those images show the high resolution patterning of 3-D nanostructure using nanoimprint lithography.

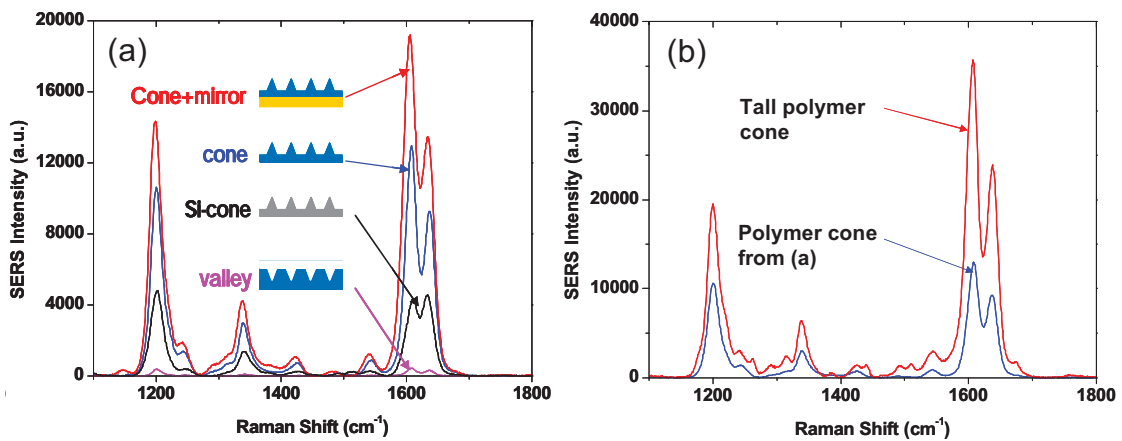


Fig.2 (a) SERS spectra of trans-1,2-bis(4-pyridyl)-ethylene (BPE) molecules absorbed on Si nanogras sensor (black), nanoimprinted polymer “reversed” nanogras sensor (purple), nanoimprinted polymer nanogras sensor (blue), and polymer nanogras sensor integrated with a mirror underneath (red). The same Si nanogras was used as the master mold. (b) SERS spectra of BPE molecule absorbed on nanoimprinted polymer nanogras sensors with different height: the height optimized for Si nanogras sensor (blue, it is the same blue curve in a) and a taller one (red). It shows another factor of 3 improvement by optimizing the height.