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# Batch Fabrication of Nanopillars for Autonomous Nanofluidic SERS Arrays

Michael S. Pio, Sunghoon Kwon, Yang-Kyu Choi, and Luke P. Lee
Berkeley Sensor and Actuator Center, Department of Bioengineering
University of California at Berkeley, Berkeley, CA 94720, U. S. A.

## ABSTRACT

We have investigated a nanopillar-based surface enhanced Raman scattering (SERS) for future multiplexed nanofluidic SERS (nanoSERS) arrays. Without using e-beam or focus ion beam method, we have accomplished this simple and batch processed nanoSERS arrays on a chip, which is economical and mass producible. The polysilicon nanopillar structures are fabricated on top of a silicon wafer using optical lithography, reactive ion etching and passivation steps. High aspect ratio pillar-like nanostructures and spacing are controlled by the reactive ion etching gas and passivation steps. The heights of nanopillars ranged from 0.1 $\mu$m to 0.3 $\mu$m and their diameters ranged from 20 nm to 100 nm. A thin gold (10-20 nm) layer is evaporated on top of the nanopillar surfaces for further surface enhancements. The Raman shifts were measured for $10^{-3}$ M of 4, 6-diamidino-2-phenylindole dihydrochloride dye in solution using a 500 *mW* near infrared laser (785 nm). A direct correlation between the density of nanopillars and the intensity of Raman enhancement is observed. The SERS spectra through thin Pyrex™ glass and polydimethylsiloxane (PDMS) are characterized to find the optimized nanofluidic materials for an autonomous multiplexing biomolecular detection schemes.

## INTRODUCTION

With the recent explosion of genomic and proteomic information, there is an increasingly important need for fast, efficient, inexpensive and multiplexing biomolecular detection schemes [1]. Current biological detection methods are still encumbered by conventional labeling such as fluorescence, radioisotope, and enzymatic methods while Raman spectroscopy can identify biomolecules without any labeling by examining signatures from vibration spectra [2-4].

Surface-Enhanced Raman Scattering (SERS) is an increasingly appealing detection method for various biosensor applications because of its dramatic enhancement of Raman signals, which eventually increases the detection limit of the sensing system. In one example, researchers have combined SERS and Capillary Electrophoresis (CE) to avoid fluorescence labeling and also to obtain structure specific information [4]. Several research groups have reported single molecule detection and spectroscopy using SERS [5-6]. Up to $10^{14}$ enhancements have been reported using silver colloidal solution [4]. Other researchers have used annealed gold films to attain Raman enhancements [7]. Most of these methods have limited mass production value as well as low controllability of feature sizes for integrated nanoSERS arrays. Any future analytical device should be able to feature nano-scale surface structures with precisely controllable features inside microfluidic environments.

This huge enhancement factor is critical in light of many biopolymers such as DNA having weak Raman signals. In addition, the exact enhancement mechanisms are not well understood as of yet. Accordingly, the various surface features giving rise to significant optical surface enhancement of the Raman signal are not well known. In order to make useful SERS surfaces which can be integrated in future detection devices, a systematic study of the relationship

between surface features and enhancement factor is needed to incorporate optimal surface to multiple target molecules. We have initiated such a study by fabricating nanopillars with various controllable structural densities and spacings on the bottom of microfluidic channels in order to develop multiplexed fast and autonomous nanoSERS arrays.

It is important to investigate the batch fabrication of nanopillars on a wafer and its feasibility to integrate with micro- or nanofluidics and micro-optical components for a fast-and reliable autonomous biomolecular detection system. Typically, SERS signals need to be measured at or near the first monolayer of molecules adsorbed onto the nanostructures. Hence, a scanning microconfocal scheme is ideally suited to probe the Raman surface to find the highest intensity signals.

In this paper, the fabrication of nanopillar structures and the characterizations of SERS on different nanopillar surfaces are described. We demonstrated high aspect ratio pillar-like nanostructures without using e-beam or focus ion beam. The spacing of nanopillars is controlled by the reactive ion etching gas and passivation steps. A set of nanopillar structures with varying surface densities are tested for their ability to enhance Raman signals of $10^{-3}$ M DAPI dye. In order to test the compatibility of different materials for the integration of nanoSERS arrays, we also measured the SERS spectra of DAPI under Pyrex™ glass and PDMS.

**Autonomous NanoSERS Arrays**

Figure 1 shows the conceptual diagram for the hybrid integration of nanoSERS arrays for future ultrafast biochemical analysis system. The nanoSERS biophotonic system consists of a substrate with different nanostructures, nano-& microfluidic channels, microlens scanner, and micro-spectrometer. Different samples flow though separate microfluidic channels and interact with different nanostructured surfaces.

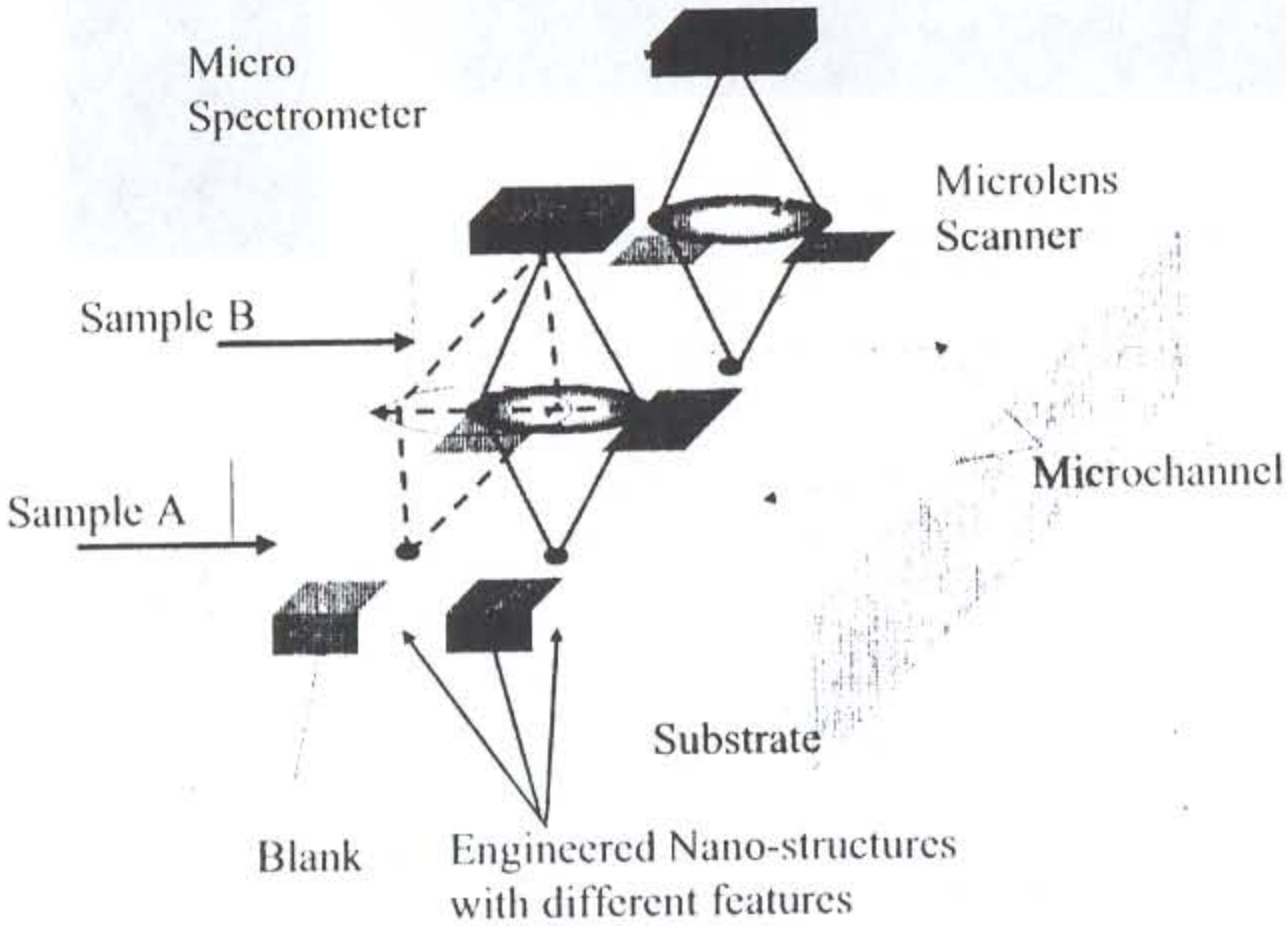


***Figure 1.*** *Conceptual schematic of nanoSERS array biophotonic system.*

The microlens scanner, which is a miniaturized moving lens system using MEMS technology, scans the focus for excitation light on nanostructures with different surface features, which will be optimal surfaces for different target molecules. The Raman scattered signal is gathered back to micro-spectrometer with same optical path with excitation ray path. Because the Raman shift signal from different nanostructured surface and control blank can be acquired with minimum variation of experimental parameter within same fluidic channel and with same optics, the nanoSERS enables a systematic study of SERS by comparing the signals from each surface, large number of sensible reagent by placing various nanostructures, and furthermore, high throughput screening of samples due to multiple of nano- & microfluidic channels and detectors on same substrate.

## MATERIALS AND METHODS

Nanopillars were formed with a 200 sccm of HBr, 7 sccm of $O_2$, 35 mTorr of pressure, 250 W of top power, and 120 W of bottom power with Lam Research 9400 TCP etcher. An etch rate of poly-silicon with HBr showed 450 nm/min and (200:1) selectivity of poly-silicon to oxide. Thus, 100-200 nm height nanopillars were formed with timed etch. The role of HBr is to etch silicon and the role of $O_2$ is to passivate it. At this point, byproduct of silicon oxybromide will serve as nanomasks and pillars will appear because of highly directional etching.

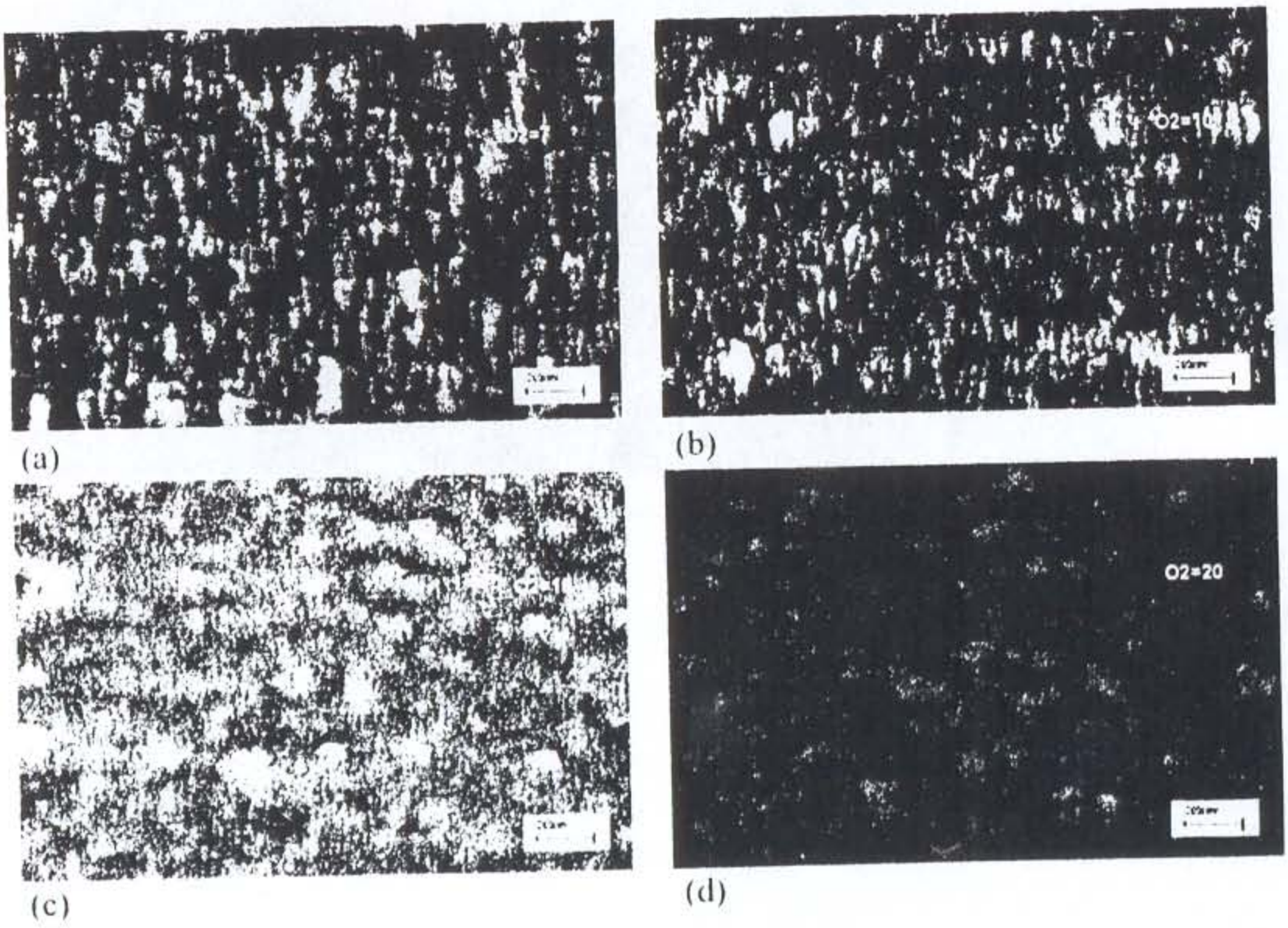


***Figure 2.*** *SEM pictures of the nanopillar structures as the $O_2$ content is varied in the Lam Research 9400 TCP etcher: (a) $O_2$ = 7 sccm, (b) $O_2$ = 10 sccm, (c) $O_2$ = 15 sccm, and (d) $O_2$ = 20 sccm.*

These pillars are passivated with thin silicon oxybromide. $O_2$ acts as oxidant to generate $Si_xO_yBr_z$. They put on the wafer again and serve as nano-masks to stop etching silicon beneath them. They became taller as etching time increased. Recently, we found that densities and diameters of nanopillars are controlled by the ratio of HBr and $O_2$. $O_2$ contents are changed from 7 sccm to 20 sccm while all other etch parameters are fixed. As $O_2$ content is increased, the density of nanopillars increased. However, nanopillars were merged together and changed to smooth surface again beyond a 15 sccm of $O_2$. After the nanopillars are fabricated on top of the silicon surface, a thin 15-20 nm film of gold was deposited over the structures using Veeco evaporating system. In the future, other materials such silver will be deposited on top of the nanopillars. Figure 2 shows SEM images of the nanopillars. These SEM images show the different densities of nanopillar structures as the $O_2$ content is varied.

All SERS spectra were measured using the Raman Systems R2001™ spectrometer equipped with an InPhotonics RamanProbe™ fiber optic sampling probe. The probe which features integrated dichroic filters, mirrors, and lenses was mounted on a ring stand by two 3-pronged clamps. The excitation and detection optical paths are connected to the ends of two separate fibers, one for delivering 500 *mW* (785 nm) high-output laser and the other for detecting Raman scattering events. The focal distance of the lens system is 5mm from the tip of the probe and the spot size is approximately 90 $\mu$m in the lateral direction and 100 $\mu$m in the vertical direction. The spectrometer features a 2048 element silicon CCD array with 1-second minimum integration time. All spectra were taken using R2001 software and analyzed with GRAMS/32 AI from Galactic Industries Corporation.

## RESULTS and DISCUSSIONS

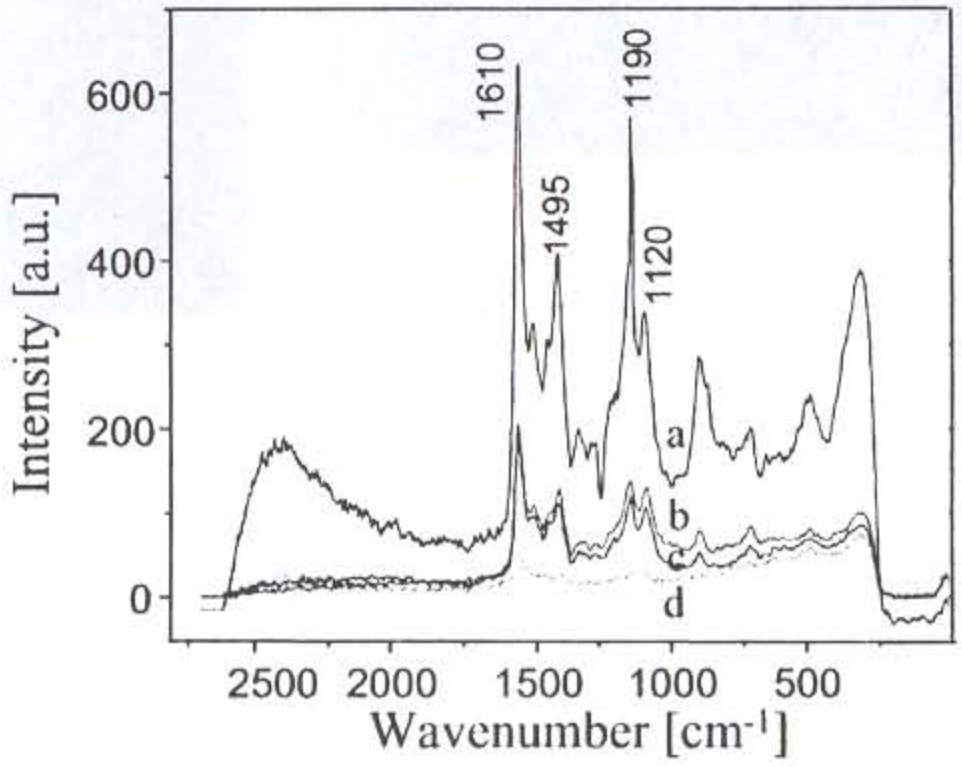


***Figure 3**. The Raman spectra of 1mM DAPI on nanopillar structures. Each sample was etched with different $O_2$ passivation content: (a) 7 sccm, (b) 10 sccm, (c) 15 sccm, and (d) 20 sccm. All spectra are 2-second integrations.*

Figure 3 shows the Raman spectra of DAPI enhanced by the nanopillar structures. Typical DAPI peaks are located at 1610, 1495, 1190 and 1120 $cm^{-1}$ [8]. Figure 4 compares the typical Raman enhancement of nanopillars versus gold on top of bare silicon.

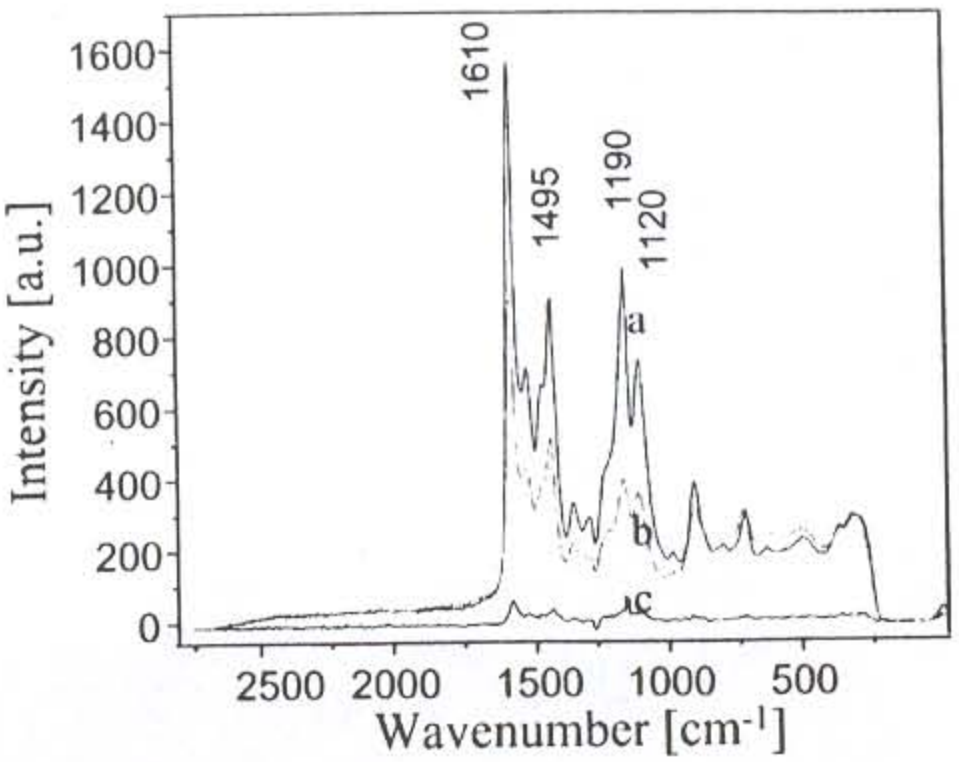


***Figure 4.*** *Raman enhancement was observed for the nanopillar substrates: (a) nanopillars, (b) gold coated bare-silicon, and (c) no substrate. All spectra are 1-second integration.*

In order to test the compatibility of different materials for microfluidic integration, we also measured the Raman signal of DAPI under thin Pyrex™ glass and PDMS (Fig. 5). There was no serious degradation of the DAPI Raman signal by the examined materials. Future nanoSERS arrays will need a transparent substrate for nano- & microfluidic channels in order to measure the SERS spectra.

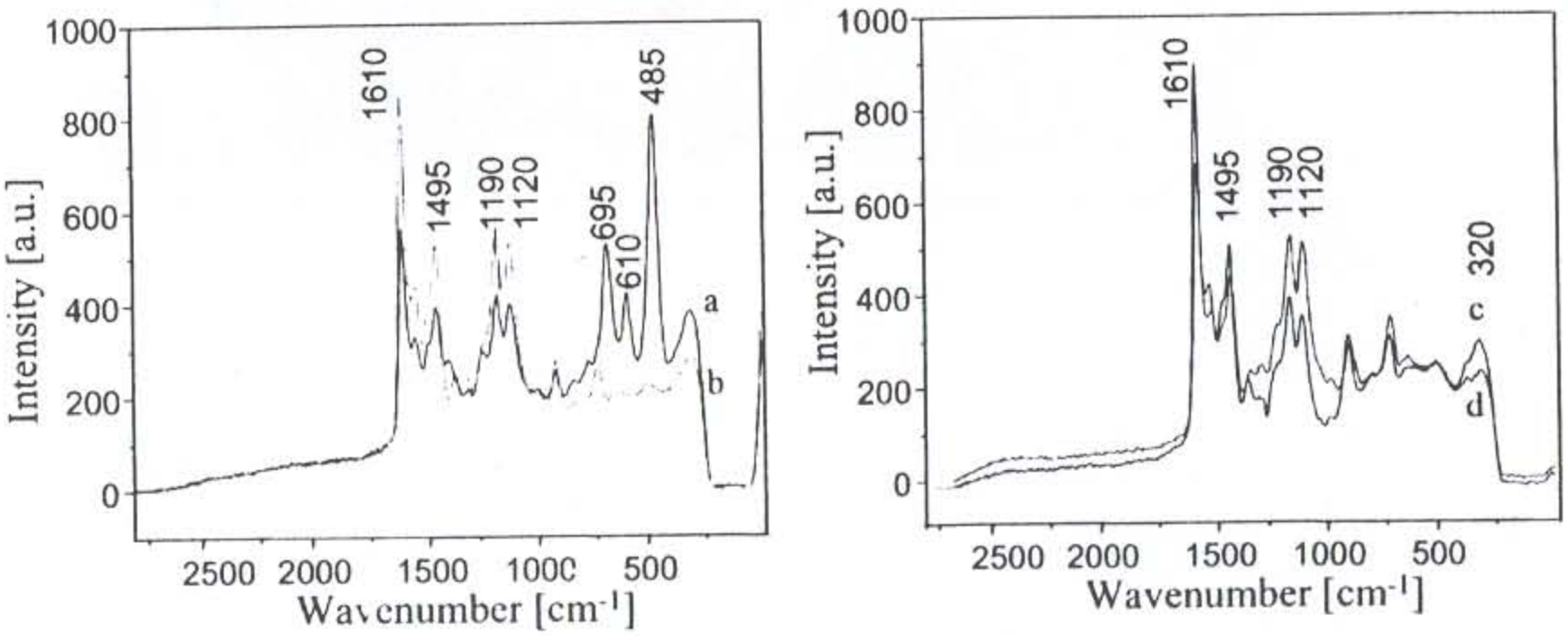


***Figure 5.*** *Raman spectra of DAPI on nanopillars with nano- & microlfuidic materials: (a) PDMS on top of nanopillars, (b) & (c) only nano-pillars, and (d) Pyrex™ on top of nanopillars. All spectra are 1-second integrations.*

Figure 3 shows that there is a direct relationship between $O_2$ passivation concentration, which produce different nanopillar densities as seen by Figure 2, and intensity of enhanced Raman signals. The highest Raman intensity was observed for $O_2$ passivation concentration of 7 sccm. The lowest signal was measured at 20 sccm. The overlay plot of the different density nanopillars suggests that there is a general trend in the range of 7-20 sccm, which can be controlled during fabrication steps. DAPI molecules typically have the highest intensity peak at 1610 $cm^{-1}$. Figure 4 compares the relative enhanced Raman signal of the nanopillars and bare silicon surface, both coated with 20 nm of gold. Both samples display enhancement when compared with DAPI in solution. The nanopillar densities increase as $O_2$ content increases until a peak density is reached and the structures merge together to form a smooth surface. A systematic study of the effects of nanopillar surface densities and aspect ratios will be pursued in the future.

## CONCLUSIONS

Nanopillar surfaces have been fabricated using batch process and coated with 20 nm of gold. The $O_2$ content during passivation step was controlled to generate nanopillars with varying densities. A direct relationship between $O_2$ passivation concentration, which produce different nanopillar densities, and intensity of enhanced Raman signals is observed. The highest Raman intensity was observed for $O_2$ passivation concentration of 7 sccm. The nanopillars also show enhanced Raman signal when compared to similarly gold-coated bare silicon. Pyrex™ and PDMS were initially tested for their compatibility as nano- & microfluidic components in future integrated nanoSERS-based biomolecular detection system.

## ACKNOWLEDGMENTS

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