Nanorough gold for enhanced Raman scattering

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Conventional Raman scattering is a workhorse technique for detecting and identifying complex molecular samples. In surface enhanced Raman scattering, a nanorough metallic surface close to the sample enhances the Raman signal enormously. In this work, the surface is on a clear epoxy substrate. The epoxy is cast on a silicon wafer, using 20 nm of gold as a mold release. This single step process already produces useful enhanced Raman signals. However, the Raman signal is further enhanced by (1) depositing additional gold on the epoxy substrate and (2) by using a combination of wet and dry etches to roughen the silicon substrate before casting the epoxy. The advantage of a clear substrate is that the Raman signal may be obtained by passing light through the substrate, with opaque samples simply placed against the surface. Results were obtained with solutions of Rhodamine 6G in deionized water over a range of concentrations from 1 nM to 1 mM. In all cases, the signal to noise ratio was greater than 10:1. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4826701>]

I. INTRODUCTION

Conventional Raman scattering is a workhorse technique for detecting and identifying complex molecular samples. The presence of a nanorough metallic surface in close proximity to the sample has been shown to enhance the scattered Raman light signal enormously.^{1–5} This paper reports several techniques for obtaining nano-rough gold surfaces on a transparent substrate using simple apparatus and no lithographic steps, thus making it available to a wide range of more modestly equipped laboratories. The advantage of a clear substrate is that the Raman signal may be obtained by passing the laser light through the substrate to the sample. This permits the use of opaque and/or remote samples to which the laser light is directed.

II. EXPERIMENT

In the simplest approach, approximately 20 nm of gold was sputtered on the polished surface of a silicon wafer. Gold was chosen over silver, which also has surface-enhanced Raman scattering (SERS) properties, for its long term stability and poor adherence to silicon. A drop of UV curing epoxy⁶ was placed on the wafer and mechanically spread to a thickness of about 0.5 mm by pressing with a flexible plastic foil. The epoxy chosen is ordinarily used as a “lens bond” to cement optical components and is transparent at visible wavelengths. When the epoxy was hardened, after about 5 min under a 13 W UV lamp, the foil and then the epoxy were readily peeled off the silicon wafer. Gold’s poor adherence facilitated the peeling by acting as a mold release. Some gold remained on the epoxy as a noncontinuous layer. The transmission of the gold covered epoxy was about 35%. This single step process produced useful enhanced Raman signals. However, sputtering additional gold directly on the epoxy further enhanced the Raman scattering signal.

The Raman scattering signal was enhanced even more by etching the silicon wafer to roughen its surface before the gold was deposited. The etching was either a dry, reactive ion etch or the combination of a wet etch followed by the dry etch. The reactive ion etch used SF₆ to remove about 200 nm of silicon.

The wet etch was in an electric field on highly doped (0.001 Ω·cm) p-type (100) silicon wafers. They were etched for 3 min in a 3:7 solution of HF in ethanol in a cell 21 mm in diameter and 47 mm long (Fig. 1).⁷ A voltage of 3.5 V was applied to the cell. The etched area was defined by a 25 mm diameter O-ring and a Teflon block, resulting in a current density of 13 mA/cm². The etching started as closely spaced narrow holes which were undercut as the holes deepened. The subsequent reactive ion etch in SF₆ (200 W for 10 s) exposed the wider subsurface openings, further roughening the silicon surface. Figure 2(a) shows a 1 kV scanning electron microscope (SEM) image of the surface of a wafer after the wet etch, and Fig. 2(b) shows a similar area after the subsequent reactive ion etch. 1 kV SEMs were also taken of the epoxy substrate after additional gold deposition [Figs. 2(c) and 2(d)]. Because the epoxy was cast on the silicon, the images might be expected to be complementary. However, they are very different. This difference arises in

Fig. 1. Apparatus for etching the silicon. The etch was a 3:7 mixture of 48% HF acid in ethanol. The typical etching time was 3 min at room temperature.

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FIG. 2. (a) SEM of the surface of a silicon wafer after wet etching as in Fig. 1. (b) Similar area on the wafer after subsequent reactive ion etching in SF_6 . (c) Epoxy substrate cast on dry etched wafer and covered with 60 nm of gold. (d) Epoxy substrate cast on both wet and dry etched wafer and covered with 60 nm of gold. All the above SEM images were taken at a beam voltage of 1 kV. (e) SEM image at 3 kV of epoxy substrate cast on both wet and dry etched wafer and covered with 40 nm of gold.

part because the electron range in gold is only about 1/8th its range in silicon. The electron range at 3 kV in gold is comparable to the range at 1 kV in silicon and an image of the gold surface at 3 kV, taken with a different SEM, more nearly complements the 1 kV silicon image [Fig. 2(e)]. Although the 1 kV images indicate the presence of very small features in the gold, uncertainties in the image formation of the two SEMs preclude a direct depiction of the gold surfaces. However, this was obtained with an AFM (Fig. 3). The wet and dry etched sample is much rougher, with an RMS height variation of 32 nm on the wet and dry etched wafer and 14 nm on the wet etched wafer. The corresponding peak to valley

FIG. 3. AFM images of 40 nm of gold on epoxy substrates cast on (a) dry etched wafer and (b) both wet and dry etched wafer. The height distributions across the marked 1 micron lines are shown below. The RMS height variation was 32 nm on the wet and dry etched wafer and 14 nm on the dry etched wafer.

variation is 600–250 nm. The greater roughness of the wet and dry etched wafer increases the plasmon enhancement.

Test cells were constructed in which the clear epoxy substrates were sandwiched between a microscope slide and a cover slip (Fig. 4). The active volumes of the cells were about 0.1 mL. They were filled and emptied via 1 mm ID stainless steel and rubber tubes. Rhodamine 6G was used as a test material, and solutions of it dissolved in deionized (DI) water were pumped through the cells from a syringe.

Raman spectra were obtained with a Raman spectrometer⁸ operating with a 1 mW 633 nm laser beam and a 5 s integration time. A 50× NA = 0.55 long working distance microscope objective⁹ was used to focus either on the front surface of the gold through the microscope slide and the Rhodamine 6G solution, or on the back surface of the gold through the cover slip and the clear epoxy substrate (Fig. 4). Stock solutions of Rhodamine 6G were prepared, ranging by factors of 10 in concentrations from 1 nM to 1 mM. To minimize possible contamination of the cells the solutions were studied in order, from the lowest concentration to the highest. At least 1 mL of each solution was pumped through the

FIG. 4. Test cell. The microscope objective is shown focusing light from the Raman spectrometer onto the gold surface of the epoxy substrate. Turning the cell upside down focuses the light through the cover slip and the epoxy substrate. The cell is filled with a solution of Rhodamine 6G.

FIG. 5. Backgrounds due to materials used in the construction of the cells. The strongest signal is from light focused on the epoxy substrate, but the peak at 1362 cm^{-1} is absent.

cells to flush out any remaining solution of the lower concentration.

III. RESULTS AND DISCUSSION

Contributions to the Raman scattering signal arising from the materials used to construct the cells were evaluated by obtaining Raman spectra with the cells both empty and filled with DI water. Background signals for the empty and water filled cells were obtained with the spectrometer focused on the front surface of the gold (Fig. 5). The signal from the epoxy was obtained with the spectrometer focused on the back surface of the gold, through the epoxy. None of the background signals showed a peak at 1362 cm^{-1} , the reference peak that was used as a measure of the Rhodamine 6G signal.^{10,11}

The strongest Raman scattering signals were obtained with light focused through the solutions to the surface of the epoxy substrate on which an additional 80 nm of gold had been sputtered (Fig. 6). Signals were obtained over the full range from 1 nM to 1 mM for all three methods of preparation of the epoxy substrate (Fig. 7). However, they were strongest for the epoxy cast on double etched silicon wafers. Below $1\text{ }\mu\text{M}$ the spectrum from epoxy cast on smooth, unetched, wafers changed^{12–14} (Fig. 8) but the reference peak at 1362 cm^{-1} remained.

Surface enhanced Raman scattering was observed for light focused through the solutions to the gold surface even

FIG. 6. Signals obtained with 80 nm of gold in contact with the Rhodamine 6G solutions. The gold was deposited on an epoxy substrate that was cast on a silicon wafer that had been both wet and dry etched. The Rhodamine 6G concentrations vary over a factor of 10^6 , from 1 mM to 1 nM.

with no additional gold added to the epoxy substrate. These signals evidently arose because some of the gold used for mold release adhered to the epoxy. Sputtering additional gold significantly increased the observed signal strengths (Fig. 9).

Light entering through the epoxy side of the sample must make two passes through the gold. The measured

FIG. 7. Effects of etching the silicon wafer from which the epoxy substrate was cast. Stronger surface enhanced Raman signals, measured at the 1362 cm^{-1} line, were obtained after etching. The dotted curve reflects a change in spectrum at lower concentrations for the not etched case—see Fig. 8 for details.

FIG. 8. Surface enhanced Raman spectra obtained with no preliminary etching of the silicon wafer from which the epoxy substrate was cast.

FIG. 9. Effect of additional gold on the surface enhanced Raman signal. Signals from Rhodamine 6G concentrations less than 10 μ M required at least 50 nm of gold to be observable.

FIG. 10. Surface enhanced Raman signals from Rhodamine 6G solutions viewed through the transparent substrate.

transmission was about 30% per 20 nm of gold. It was slightly higher for 20 nm or less of additional gold deposited on epoxy cast over roughened silicon, although that interface appeared dark when viewed through the epoxy. Useful signals were only obtained in the range of concentrations from 10 μ M to 1 mM (Fig. 10).

IV. SUMMARY AND CONCLUSIONS

Surface enhanced Raman scattering requires a metallic surface that is rough at the nanoscale. This work demonstrates how such surfaces may be obtained on a transparent substrate with minimal effort. The transparent substrate was a UV curing epoxy cast on a silicon wafer. A layer of gold sputtered on the wafer acted as a mold release because the adherence between the epoxy and the gold was better than that between the gold and the silicon. The gold was sufficiently rough to enhance Raman scattering from a solution of Rhodamine 6G dye. Pre-etching the silicon wafer, with wet and/or dry etches, increased the roughness of the wafer and the epoxy, and therefore the strength of the Raman signal. Additional gold deposited directly on the epoxy also increased the Raman signal. Signal to noise ratios of greater than 10:1 were obtained with solutions of Rhodamine 6G down to 1 nM.

Simple cells were described in which light from a Raman spectrometer was focused both through the Rhodamine 6G solutions and through the epoxy substrate. The advantage of a clear substrate is that it can be placed at the end of a probe instead of in a cell. However, since the light must pass through the gold in this configuration, the thickness of any additional gold is limited. This probe can then be placed against, or inside, the specimen whose Raman spectrum is to be studied. Work is continuing on the incorporation of the techniques developed here into an endoscopic probe.

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