Preparation of silicon surface pyramid arrays and modification of thin gold film for surface-enhanced Raman scattering

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Abstract. Monocrystalline silicon surface microstructure is prepared by 15wt% K$_3$PO$_4$ and 3wt% K$_2$SiO$_3$ solutions at 90 °C for 42 min. The monocrystalline silicon surface microstructure obtained high coverage, uniformity and low reflectivity. The surface-enhanced Raman scattering (SERS) substrate based on silicon nanoporous pyramid arrays/gold film (Si/Au) is prepared by ion sputtering. Methylene blue (1×10$^{-5}$mol/L) is used as a probe molecule, and the enhancement effect of Si/Au SERS substrate is investigated. The results show that silicon surface pyramid arrays have high Raman enhancement effect when deposition time is 5min. Furthermore, the applied of the Si/Au SERS substrate in Raman detection of melamine (1×10$^{-3}$mol/L), the Raman characteristic peaks of melamine is enhanced obviously. These results indicated that the Si/Au SERS substrate had potential application value in food safety and the detection of chemical dyes and contraband.

1. Introduction
Surface Enhanced Raman Scattering (SERS) technology has been widely used in physics, materials science, biology and environmental science [1, 2]. In 1974, Fleischmann et al. study the Raman scattering experiment for the first time using pyridine as the Raman active material on the silver electrode [3]. It was found that the enhanced Raman scattering signal of pyridine was obtained on the rough silver electrode surface. With the rough surface, the silver electrode could adsorb more molecules and then emerged the enhancement effect of Raman scattering. In 1977, through theoretical and experimental observations, Van Duyne et al. found that the Raman scattering which was generated by the pyridine molecules adsorbed on the surface of the silver electrode was enhanced by 10$^5$ to 10$^6$ times compared to the normal Raman spectrum [4]. The pyridine molecules can be adsorbed on rough metals (gold, silver, copper) surface, and rough metal surface facilitates the excitation of surface Plasmon [5].

The SERS phenomenon is also observed on other rough metal surfaces, such as vacuum-evaporated metal island films, chemically prepared metal sols, coating metals film and etc. Guina Xiao and his team prepared SiO$_2$-Au core cap nanostructure arrays on glass substrates by dip coating and wet chemical reduction [6]. Bo-Kai Chao prepared a high SERS substrate in which plasma gold Nanodroplets are fabricated by wet etching and island photolithography [7]. K. Leinart sedimentated a layer of aluminum (100-500nm) thin film on a (100) oriented Si wafer by magnetron sputtering [8].
Zhang prepared large-area and highly uniform Si nanotaper array modified with Ag or Au/Ag nanoparticles as a Raman substrate [9]. Another important application of the metal SERS effect was the probe tip of the metallized film.

In this paper, a method for preparation of Raman substrates is reported. Using 15wt% K₃PO₄ and 3wt% K₂SiO₃ solutions at 90 °C for 42min, the monocrystalline silicon surface microstructure with small size, high coverage, and good uniformity is prepared by anisotropic etching on the monocrystalline silicon surface [10, 11]. The Si/Au SERS substrate is prepared by ion sputtering. In order to optimize the substrate enhancement effect, the influence of sputtering gold film thickness is discussed. MB is selected as the probe molecule, and measure the SERS activity of melamine. There are compared with MB and melamine on normal Raman spectra and their SERS adsorbed on Si/Au SERS substrate.

2. Experimental

2.1. Materials

Hydrofluoric acid (HF), ethyl alcohol absolute (C₂H₆O), potassium phosphate tribasic (K₃PO₄) and potassium silicate (K₂SiO₃) are used without any further purification. Methylene blue (MB) purchased from Shanghai Xin Chemical Co. Ltd. ultrapure water is used for all solution preparation and experiments (resistivity>18.2MΩ·cm). MB solution is diluted to various concentrations of 1×10⁻⁴ mol/L and 1×10⁻⁵ mol/L with ultrapure water. Melamine solution is diluted to 0.01mol/L with ultrapure water. Monocrystalline silicon wafers of P-type, <100> oriented and size 15mm × 15mm with resistivity 1~3Ω·cm are used as the etching experiments. The UV-Vis spectra of silicon wafer surface reflectivity data are recorded using a UV-Vis spectrophotometer (SHIMADZU UV-2600) equipped with an integrating sphere. The size distribution, uniformity and morphology of monocrystalline silicon wafers are examined by FEI Company (USA) scanning electron microscope quanta 250 FEG (SEM). Raman spectra are recorded between 300 and 1800 cm⁻¹ with a 785 nm excitation Raman spectrometer (portable Raman Series, QE65Pro). Cressington 108 Auto /SE Sputter Coater (USA).

Preparation of monocrystalline silicon surface microstructure: After proper cleaning in our group’s own way [12], we used monocrystalline p-type silicon wafers, oriented <100> and size 15mm×15mm to prepare pyramid structure of silicon surface by chemical wet etching method. We maintained the temperature at 90 °C in the whole process. Two steps are as follows: (1) As-cleaned silicon samples are dipped in the capped vessel containing 15wt% K₃PO₄ and 3wt% K₂SiO₃ solution for 36min to etch [13]. (2) After completing the etch process, monocrystalline silicon wafers are washed into ethanol and ultrapure water, and cleaning in ultrasonic cleaner for 5min, respectively. Finally, the etched samples are rinsed in ultrapure water and then drying in the oven.

Preparation of Si/Au SERS substrate: Using the physical method of ion sputtering deposits gold film on silicon surface pyramid arrays, and the sputtering time is 3min, 4min, 5min, 5.5min and 6min, respectively. As a result, the uniformly decorated Au nanoparticles on pyramid arrays are achieved. In order to keep the same thickness of gold film, each silicon wafer is kept in the same sputtering position of the sputtering process. Fig. 1 shows the fabrication of Si/Au SERS substrate.
3. Results and discussion

The SEM images of the monocrystalline silicon wafers surface microstructure are shown in Fig. 2. It is exhibited that the pyramid with small size, high coverage, and good uniformity. Fig. 3 shows the distribution of the pyramid size under the etching process condition 15wt% K₃PO₄ and 3wt% K₂SiO₃ solutions at 90 °C for 36min. We clearly discovered that most pyramids size are between 2μm to 6μm. With the size of the average size of the pyramid is 4.8μm. Furthermore, the density of pyramid is 92.8%, and the pyramid size distribution range is 0.97~11.39μm.

![Figure 2](image)

Figure 2. SEM images of monocrystalline silicon wafers surface microstructure with 15wt% K₃PO₄ and 3wt% K₂SiO₃ solutions at 90°C etching time for 36min.

![Figure 3](image)

Figure 3. Distribution of pyramid size for etching time 36min.

![Figure 4](image)

Figure 4. Reflectance curve of silicon wafers: (a) Monocrystalline silicon surface; (b) Monocrystalline silicon wafers etched surface; (c) Si/Au SERS substrate
Fig. 4 (a) is the silicon surface reflectance spectrum, (c) is the silicon wafer etched surface reflectance spectrum, and (b) is the silicon wafer surface with the coated gold film reflectance spectrum. It is worth noting that the spectra of (a) and (c) are very similar, and the surface reflectivity of (c) is reduced. Fig. 4 (b) reflectance between 380 and 550nm are reduced. The SEM image of Si/Au SERS substrate at different magnifications is shown in Fig. 5 as expected, the Si/Au SERS substrate still retains the pyramid structure. From the enlarged SEM image, we can observe that the gold film roughens the pyramid surface. It’s got more hot spots for Si/Au SERS substrates. This roughened pyramid surface is greatly enhancing the Raman signal.

![SEM image of Si/Au SERS substrate at different magnifications](image)

**Figure 5.** The images of SEM the Si/Au substrate under different magnification.

In order to obtain the best Si/Au SERS substrate, we studied the different coating times on the silicon etched surface. The thickness of gold film can be controlled by sputtering time. MB, a phenothiazinyl dye, was used as a probe molecules to demonstrate the property of the substrate. We dropped MB aqueous solution with concentrations $1 \times 10^{-5}$mol/L on the surface of Si/Au SERS substrate, then dried in the air naturally. Fig. 6 is the SERS spectrum of the MB for comparison. Curves a, b, c, and d shows the only part characteristic peaks of the MB. It can obviously show the characteristic peak of MB well and the characteristic peak 520 cm$^{-1}$ of the silicon wafer is quenched in curve c. The optimal sputtering time was 5min.

![SERS spectrum of MB](image)

**Figure 6.** Methylene blue (MB) $1 \times 10^{-5}$mol/L adsorbed on Si/Au SERS substrates prepared at different sputtering times with a: 3min, b: 4min, c: 5min, d: 5.5min, e: 6min.
Figure 7. (a) Normal Raman scattering spectrum of $1 \times 10^{-4}$ mol/L MB aqueous solution, (b) S of methylene blue $1 \times 10^{-5}$ mol/L adsorbed on Si/Au SERS substrate.

The normal Raman spectrum of MB with integration time of 20s and SERS spectrum that the MB molecules are adsorbed on the Si/Au SERS substrate, which are shown in Fig. 7 curve (a), (b). Curve (a) shows part of characteristic Raman bands of MB molecules. All of the vibrational modes of characteristic peaks of MB molecules are obviously shown in curve (b). The background fluorescence of the curve b at 520 cm$^{-1}$ with the silicon wafer itself has been eliminated. The peak Raman shifts, relative intensity and peak attribution of methylene blue are listed in Table 1, compared with the results reported in the literature [14]. The SERS spectrum of MB on these substrates consists with those of references, part of the positions of vibrational peaks occur shifting. No peak attribution can be found for 1326, 1227, 1151 and 949 cm$^{-1}$. It may cause by the interaction between probe molecules and the Si/Au SERS substrate. The other reason is that the scattering light may be affected by the intensity [13]. The characteristic peak of 447 cm$^{-1}$ of MB absorbed on the substrate is matched with the corresponding MB aqueous solution. However, the bands at 773, 1187, 1304, 1407 and 1630 cm$^{-1}$ in the Fig. 7 (curve a) spectrum are shifted to 771, 1182, 1326, 1397 and 1621 cm$^{-1}$ in the SERS spectra, respectively. In addition at 499, 612, 667, 888, 949, 1043, 1121, 1151, 1227, 1418 and 1502 cm$^{-1}$ does not appear in normal Raman spectrum of MB. However, the peak intensities of MB adsorbed on Si/Au SERS substrate are stronger than those MB normal Raman spectrum, especially the peak at 447, 771, 1397 and 1621 cm$^{-1}$. Therefore, this substrate enhances the Raman signal and eliminates fluorescence interference effectively.
**Table 1.** Raman shifts, relative intensity and peak attribution of methylene blue†.

| Aqueous solution/cm\(^{-1}\) | Si/Au substrate/cm\(^{-1}\) | Reported result/cm\(^{-1}\) | Band assignment |
|-------------------------------|-----------------------------|-----------------------------|-----------------|
| 1630                          | 1621 (s)                    | 1617 (s) [15]               | \(\nu(C\text{―}C)\) |
|                               |                             | 1597 (w) [16]               | \(\nu(C\text{―}C)\) |
|                               | 1502 (w)                    | 1513 (w) [16]               | \(\nu\_\text{asym}(C\text{―}C)\) |
|                               | 1418 (s)                    | 1427 (m) [14]               | \(\nu\_\text{asym}(C\text{―}C)\) |
| 1407                          | 1397 (s)                    | 1396 (m) [15]               | \(\alpha(C\text{―}H)\) |
| 1304                          | 1326 (m)                    | 1323 (w) [14]               | \(\beta(C\text{―}H)\) |
|                               | 1227 (w)                    | 1227 (w) [17]               | \(\gamma(C\text{―}H)\) |
| 1187                          | 1182 (s)                    | 1184 (m) [15]               | \(\nu(C\text{―}N)\) |
|                               | 1151 (s)                    | 1121 (m) [16]               | \(\gamma(C\text{―}H)\) |
|                               | 1043 (m)                    | 1037 (m) [14]               | \(\beta(C\text{―}H)\) |
| 949 (m)                       |                             |                             | \(\delta(C\text{―}S\text{―}C)\) |
|                               | 888 (s)                     | 888 (s) [18]                | \(\beta(C\text{―}H)\) |
| 773                           | 771 (m)                     | 771 (m) [14]                | \(\beta(C\text{―}H)\) |
|                               | 667 (w)                     | 670 (w) [17, 18]            | \(\gamma(C\text{―}H)\) |
|                               | 612 (s)                     | 612 (m) [16]                | \(\delta(C\text{―}S\text{―}C)\) |
|                               | 499 (w)                     | 502 (m) [19]                | \(\delta(C\text{―}N\text{―}C)\) |
| 447                           | 447 (s)                     | 449 (m) [17]                | \(\delta(C\text{―}N\text{―}C)\) |

Abbreviation: s, strong; m, medium; w, weak; \(\nu\), stretching; \(\alpha\), in-plane ring deformation; \(\beta\), in-plane bending; \(\gamma\), out-of-plane bending; \(\delta\), skeletal deformation.

In the same conditions, we further investigated the Si/Au SERS substrate property by detecting aqueous melamine. Fig. 8 shows the SERS signals of the Si/Au SERS substrate (curve a), melamine aqueous solution at \(1 \times 10^{-3}\) mol/L absorbed on Si/Au SERS substrate (curve b), and pure melamine powder (curve c). Fig. 8 (a) shows Raman spectrum of silicon wafers at 520 cm\(^{-1}\) can be observed easily between 400 and 1100 cm\(^{-1}\). Spectrum of 520 cm\(^{-1}\) on curve (a) is assigned to the characteristic of silicon. The curve (c) shows the Raman spectra of melamine powder. All of the vibrational modes of melamine can be observed. The peaks appearing at 583, 676, and 984 cm\(^{-1}\) are the characteristic Raman peak of melamine. The SERS spectrum of melamine aqueous solution absorbed on these substrates closely matches with Raman spectra of melamine powder. The strongest peak at 675 cm\(^{-1}\) is involving the in-plane deformation of the triazine ring, and definition to ring-breathing II mode [20]. Another strong Raman peak at 984 cm\(^{-1}\) is attributed to the ring-breathing mode of the triazine ring, and related to the ring of nitrogen atoms [21].
4. Conclusion

In this study, silicon wafer surface microstructure of pyramid arrays has been prepared by a wet chemical etching process from silicon wafer surfaces. The Si/Au SERS substrate is fabricated by the sputter gold film on the silicon wafers surface. By sputtering gold film optimum time was 5 minutes, we got more hot spots for Si/Au SERS substrates, which means the Raman enhancement effect is higher. Raman signals is detected of low concentrations of (1×10^{-5} mol/L) methylene blue and (1×10^{-3} mol/L) melamine aqueous solution, which are adsorbed on Si/Au SERS substrates, respectively. In addition, this substrate has great advantages in manufacturing and morphology controllability. These results indicate that the Si/Au SERS substrate has potential application in food safety and the detection of chemical dyes and contraband.

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