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Research on Raman Enhancement of Silicon Dioxide Substrate Modified by Different Thickness of Au Nanoparticles Based on Sensors

Qiang Zou
School of Microelectronics
Tianjin University, Weijin Road
Tianjin, China
zouqiang@tju.edu.cn

Shentong Mo
School of Microelectronics
Tianjin University, Weijin Road
Tianjin, China
moshentong678@126.com

Guohui Li
Tianjin Development Zone Aojin High New Technology co., LTD, Weijin Road
Tianjin, China
liguohui@tju.edu.cn

Bing Yu
Shanghai Yanhua Smartech Group
Shanghai, China
yubing@tju.edu.cn

***Abstract*—In this paper, a series of orthogonal experiments on the silicon dioxide (SiO_2) substrate of the fiber optic sensor are carried out. The surface modification of the substrate with different thicknesses of Au nanoparticles is carried out, and the surface-enhanced Raman spectra of the optic-based materials are studied. The Raman spectra of various cases are analyzed, and the samples are compared under different conditions. At the same time, the surface morphology and composition of the samples are observed. The mechanism of sample formation is analyzed, including the influence of various experimental conditions on the samples. The optimized conditions were selected to make the Raman enhancement factor of SiO_2 substrate reach 105 or higher, which provides a theoretical basis for the combination of surface-enhanced Raman spectroscopy and optical fiber sensing technology. It also provides guidance for materials, structures and processes in chemical quantity, especially for biomass detection by optical fiber sensing technology. Besides, the application provides an important reference value for the field of biochemistry.**

Keywords—optical fiber sensor, silicon dioxide (SiO2), ion sputtering coating, surface-enhanced raman spectroscopy, raman enhancement factor

I. INTRODUCTION

In 1973, Hesse first proposed the idea of applying fiber optic sensing to the detection of oxygen in the blood (blood gas measurements), which opened the beginning of the application of optical fiber sensing technology in the field of biochemistry [1-2]. In 1980, the world's first fiber optic chemical sensor for the determination of physiological pH was invented, which accelerated the application of optical fiber sensing technology in the field of biochemical research. With the development of nonlinear optical research and the progress of optical fiber preparation technology, fiber biochemical sensor research has made a series of major breakthroughs [3-5]. At this stage, fiber-based biochemical sensors based on fiber-optic probe, fiber Raman spectrum, fiber evanescent wave and surface plasmon resonance have been widely used to broaden the application of optical fiber technology in biochemical field. With the rapid development of biochemical research, fiber biochemical sensor research is facing new problems and challenges [6-8]. First of all, fiber research and development and production is mainly for the optical fiber communications industry without fiber optic sensing mechanism considerations. Secondly, optical fiber sensing has shown advantages in physical quantity testing, but in the chemical, biomass detection, due to the Materials, structures and processes and other aspects of the shackles, its specificity and flexibility could not meet the needs of the development of biochemical industry. However, at the same time, with the progress of nano-materials preparation technology and micro-nano processing technology, the application of nanotechnology for biochemical sensing research and its theory gradually become mature [9-10].

In the US, GE carries on bionics researches in nanotech and develops a new generation of biosensors to achieve rapid detection of various biological threats, funded by the DARPA. In Europe, the SPOT-NOSED (Single Protein Nano-biosensor Grid Array) Project combines information science and nanoscale materials and makes a breakthrough in the development of nano-biosensors based on individual olfactory receptors, supported by the FET, a subsidiary of the European Commission [11-12]. In 1974, Fleischmann roughened the silver electrode by electrochemical redox and obtained a high-quality Raman spectrum on the surface of the rough electrode. This phenomenon is caused by the increase in the effective surface area of the electrode after roughening, so that the

electrode probe molecules can detect more Raman signals [13]. Although the roughening treatment allows the electrode probe molecules to detect more Raman signals, but the surface-enhanced Raman spectroscopy (SERS) was first proposed by Van Duyne and Creighton in 1977. Using the same system, they excluded molecular concentration factors and resonance effects. The six orders of magnitude in spectrum was enhanced due to the enhanced surface effect from the surface of the rough electrode, which was called surface-enhanced Raman spectrum [14]. In recent years, Dinh has succeeded in developing a fiber optic nano-immunosensor for the detection of BPT (Benzo pyrene tetrol, a biomarker of DNA damage associated with exposure to carcinogens benzo a pyrene). The biopsy of the sensor head incorporates a specific monoclonal antibody that is capable of detecting bio-chemicals in a single cell through antigen-specific binding [15]. Fiber-optic biosensors(FOBS), as an integration of optical fiber sensing technology and modern biochemical detection methods, are always at the cutting-edge of the development of the biochemical sensor technology.

With the development of fiber-optic biosensors, combined with the efficient scattering reflection of the properties of optical fiber's microstructure, the utilization of the optical and spectroscopic techniques provides a means for the detection and analysis of biochemical signals [16-18]. For example, the application of a large number of the analysis methods for optical background in the detection process of FOBS can realize remote distributed measurement, and with the applied technology of Wavelength Division Multiplexing (WDM), FOBS can offer the possibility to the analysis of multi-targets based on a single sensor [19-21].

However, there also exists some problems to be resolved during the development of FOBS. Restricted by the materials, structures and technics, FOBS have little relation with the chemical or biological state of the samples, as a result, with its high specificity and poor flexibility, FOBS can hardly meet the demand of the rapid development of biochemical industry so that its application range is limited [22]. Meanwhile, the application of nano technology in biochemical sensing field both theoretically and practically is getting mature, which has an edge in materials and structures. In conjunction with researches on microstructures in optical fibers doped with nano materials, it is expected to improve traditional fiber-optic sensing technology to expand the application range of FOBS in biological detection.

II. Experimental

The SiO_2 substrate on the surface of the fiber optic sensor was processed, and a series of orthogonal experiments were used to screen out the best surface treatment scheme. Firstly, the different gradients of HF acid corrosion concentration (5%, 7%, 9%, 11%, 13%, 15%, 17%, 19%) were set and the same treatment was done for the glass. Then, the different gradients of HF acid corrosion time (20 min, 30 min, 40 min, 50 min, 60 min) were set, and the glass particles were treated with the same treatment. Finally, the deposition rate of different gold particles, that is, different coating thickness (20 nm, 40 nm), was treated with ion sputtering. Besides, the optimal conditions were selected and the crystal solution of 10^{-5} mol/L was tested.

III. Results and Discussion

In this experiment, the material to be tested is crystal violet solution, Au nano-particles modified the fiber optic sensor material – SiO_2 as a SERS substrate. After the completion of Raman detection, the wxd format files need to be transformed into txt format file, and then the data was imported into the Origin software to draw the following Raman spectrum. In the graph, the ordinate is Intensity, and the unit can be expressed by Counts. The abscissa is the Raman shift, usually with its relative position relative to the Rayleigh line, and the unit is the wave number cm-1. Through the above series of corrosion, nano-modification and Raman test experiments, the following Raman spectra were obtained.

The first part is crystal violet solution with 10^{-5} mol/L, and 20nm Au particle modified fiber optic sensor material - SiO_2 as the SERS substrate.

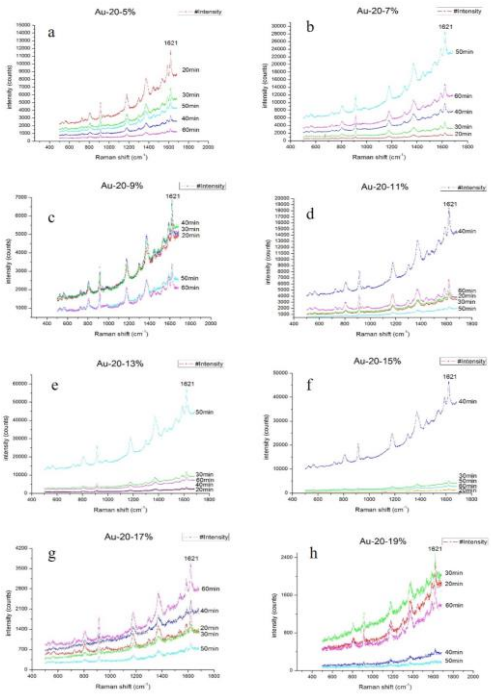

Fig. 1. 20 nm Au modification, the corrosion concentrations of the Raman spectrum are, respectively (a) 5 %; (b) 7 %; (c) 9 %; (d) 11 %; (e) 13 %; (f) 15 %; (g) 17 %; (h) 19 %

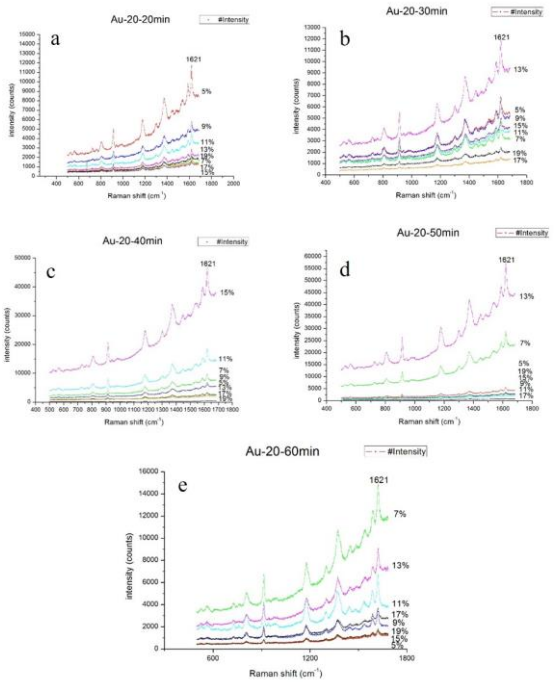

Fig. 2. 20 nm Au modification, the corrosion time of the Raman spectra is, respectively (a) 20 min; (b) 30 min; (c) 40 min; (d) 50 min; (e) 60 min

The second part is crystal violet solution with 10-5 mol/L, and 40nm Au particle modified fiber optic sensor material - SiO_2 as the SERS substrate.

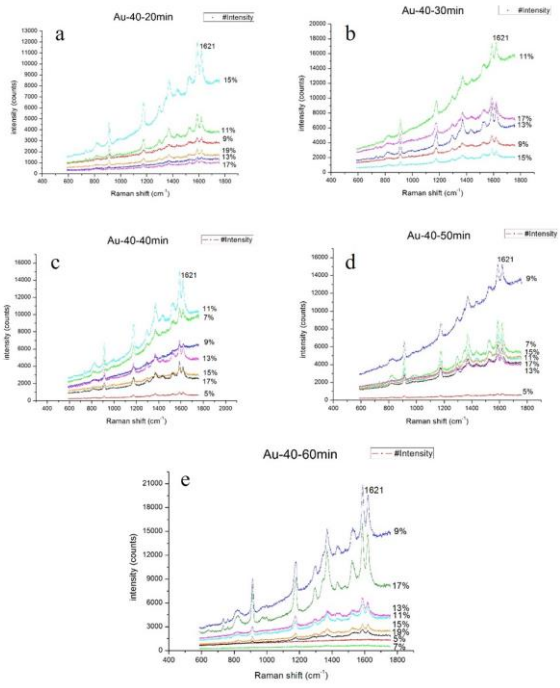

Fig. 3. 40 nm Au modification, the corrosion time of the Raman spectra is, respectively (a) 20 min; (b) 30 min; (c) 40 min; (d) 50 min; (e) 60 min

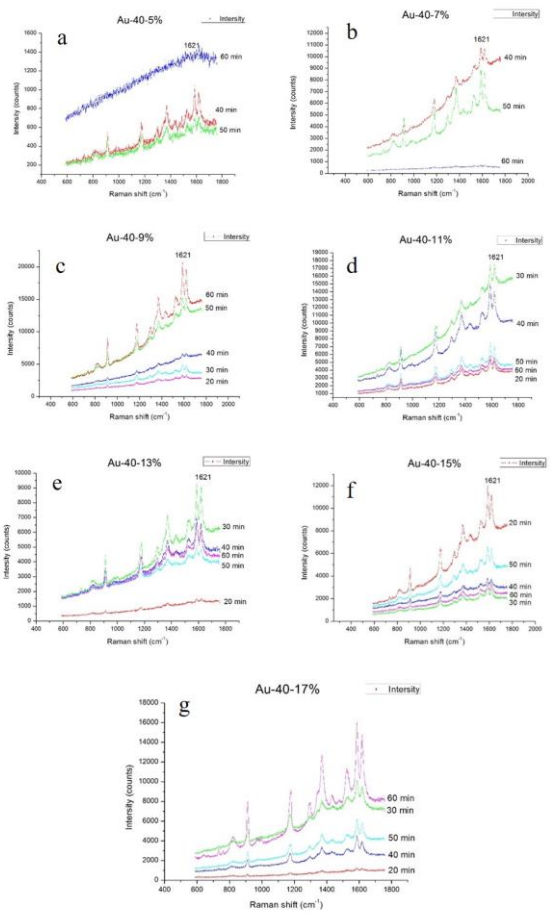

Fig. 4. 40 nm Au modification, the corrosion concentrations of the Raman spectrum are, respectively (a) 5 %; (b) 7 %; (c) 9 %; (d) 11 %; (e) 13 %; (f) 15 %; (g) 17 %

As can be seen from Fig. 1 and Fig. 4, the surface-enhanced Raman scattering intensity increases first and then decreases with the increase of the corrosion concentration. When the concentration of HF acid is between 13-15%, the surface Raman enhancement factor reaches the maximum Value. Likewise, the fiber optic sensor surface material achieves the best results. As can be seen from Fig. 2 and Fig. 3, the surface-enhanced Raman scattering intensity of the measured material increases with the increase of the etching time. Consequently, the surface-enhanced Raman scattering effect will be better.

The Raman Enhancement Factor (EF) is an important indicator of surface-enhanced Raman scattering. Most SERS tests are carried out by dropping SERS active substrate onto the glass or silicon wafer on a sample of adsorbed probe molecules.

$$\mathrm{EF} = \frac{N_{vol} I_{surf}}{N_{surf} I_{vol}} \tag{1}$$

In (1), I_{surf} is the signal intensity in the surface Raman enhancement spectrum. N_{surf} is the number of molecules reinforced in the SERS test. I_{vol} and N_{vol} are the signal intensities in the normal Raman spectrum of the material to be measured and the number of molecules. Thus, in order to measure the surface-enhanced Raman scattering effect, it is

necessary to know the number of molecules to be tested. For the test SERS of active substrate which is added to the glass flake or quartz sheet, the number of nanoparticles in the laser spot is calculated. Then, the total number of molecules is calculated by the single-layer adsorption treatment on the nanoparticles.

In this study, the measured substance was crystal violet. And its solid spectrum was large fluorescence, which caused the noise intensity to be large. However, the experimental group prepared a nano-particle modified biosensor model with a lot of experiments and tests. The SERS test of the crystal violet solution with the concentration of 10-5mol / L is related to the number of molecules reinforced in the SERS test, so the Raman enhancement factor of the biosensor model is more than 105.

IV. CONCLUSION

In summary, a biofilm sensor model with Au nanoparticles was prepared by economically simple method in this paper. The relationship between the surface-enhanced Raman scattering intensity and the surface treatment time or concentration was studied, and the best SERS effect was achieved. Its Raman Enhancement Factor reached more than 105. In order to improve the traditional optical fiber sensing technology, the SiO_2 substrate can be used to combine the microstructure of nano-materials, which will expand its application in the field of biochemical testing. As the nanotechnology has the advantages of material and structure, the substrate in the application of biochemical sensing will become increasingly mature in the future.

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