Silver Nanorods Array on the Zinc Oxide Thin Film Deposited by Hydrothermal Methods for Surface-Enhanced Raman Scattering

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Abstract: The wide application of surface-enhanced Raman spectroscopy (SERS) is based on adaptable substrates, which are primarily limited to rough precious metals and colloidal nanoparticle materials. A novel method to enhance surface Raman scattering is present. This technique is reliant on the local surface plasmon resonance phenomena, in which incident light can be coupled to the plasma at the interface, resulting in a strong electric field. The field can propagate from the surface of the metal–dielectric interface, so adjacent molecules will experience more intense Raman scattering. The physical enhancement method was adopted; silver is deposited on the surface of different pH rough zinc oxide thin film, deposited by hydrothermal methods using the above principle, considerably improving the surface Raman scattering signal. Comparing the enhancement effects of zinc oxide substrates prepared in different pH environments on the Raman effect, the optimal acid–base environment was found, and the corresponding enhancement factors were calculated.

Keywords: silver nanorods; zinc oxide; surface-enhanced Raman scattering

1. Introduction

The phenomenon of optical scattering has a special effect that is similar to the Compton effect of X-ray scattering. The frequency of light will change after scattering. “Raman scattering” implies that the molecules and photons in the substance transfer energy when a certain frequency of laser irradiates the surface of a sample [1]. According to the vibration dynamics (such as the swing and twist of atoms, as well as the swing and vibration of chemical bonds), particles change in various ways and degrees, scattering light of different frequencies. The changes of frequency are dependent on the characteristics of the scattering material. Different types of atomic groupings have different vibration modes. Therefore, the scattering light, with a specific difference from the frequency of the incident light, can be generated. The spectrum is referred to as the “Fingerprint spectrum”, which can identify the types of molecules that make up the material according to this principle [2,3]. Some bands with weak absorption or intensity change in the infrared spectrum may be strong bands in the Raman spectrum, which is conducive to the detection of these groups. In addition, the measurement range of the Raman spectrum in the low wavenumber direction is wide, which is conducive to providing the vibration information of heavy atoms. For the change of structure, the Raman spectrum is more sensitive than the infrared spectrum, and the Raman spectrum peak is clear and sharp, which is more suitable for quantitative research. Fixed samples can be determined directly without sample preparation, and can be used for qualitative and quantitative analysis without damage [4].

The surface-enhanced Raman scattering (SERS) mechanism, generally recognised in the academic community, mainly includes physical enhancement mechanisms and chemical enhancement mechanisms [5–7]. The most significant contribution is thought to be
the enhancement of the local electromagnetic field induced by the surface plasmon resonance [8]. The surface plasmon is the collective oscillation effect of the free electrons in the metal under the optical field. Due to the fact that the energy gaps of the d electrons and s electrons of the three group IB metals of Cu, Ag, and Au are larger in comparison to those of the transition metal, they are less prone to inter-band transitions [9,10]. As long as the appropriate excitation light wavelength is chosen for these three kinds of metal systems, the energy of absorbed light can be prevented from being converted into heat, owing to the occurrence of inter-band transitions, and thereby tending to realise an efficient SPR scattering process [11]. In the Raman process, the chemical interaction mostly manifests the difficulty of the electron density deformation under the optical field. When molecular chemistry is adsorbed on the surface of the substrate, surface, surface-adsorbing atoms, and other co-adsorbed species may have certain chemical interactions with the molecule. These factors have a direct impact on the electron density distribution of the molecule, as well as the system’s polarizability, which changes Raman intensity [12,13]. Chemical enhancements primarily comprise the following three types of mechanisms: non-resonance enhancement due to chemical bonding of the adsorbate to the metal substrate; increased resonance because of the formation of surface complexes (new molecular systems) by adsorbed molecules and surface-adsorbed atoms; enhanced resonance of photoinduced charge transfer of molecular metal systems by excitation light. After decades of debate, the electromagnetic enhancement mechanism is now universally regarded as the main contributor to most SERS processes [14]. Amplified light enhancement results from excitation of localised surface plasmon resonance. This light concentration is preferentially present in gaps, cracks, or sharp features of plasmonic materials that are traditionally aristocratic, and coinage metals (silver, gold, and copper) with nanoscale features [15]. The reproducible and robust structure that greatly enhances the electromagnetic field is ideal for SERS [16].

As a surface sensor measurement method based on nano scale substrate, one of the main difficulties of SERS technology focuses on the preparation and surface treatment of SERS active substrate. If the same molecule is adsorbed on solid substrates with different shapes, sizes, and morphologies, the SERS signal intensity may differ by several orders of magnitude. Therefore, the practical application depends on whether the SERS active substrate with high sensitivity, high repeatability, low detection limit, uniform hot spots, and stable physical properties can be provided. At the beginning of the advent of SERS technology, the material range of SERS active substrate was basically limited to Au, Ag, Cu nano sol particles, or the surface of Au, Ag, and Cu was chemically etched to obtain nano roughness [17,18]. Up to now, with the increasingly mature and diversified development of nano preparation technology [19], SERS substrates were expanded from a small number of B-group metals, such as Au, Ag, and Cu to transition metals, semiconductors, graphene, metal oxides and precious metals, nanocomposites, etc. [20–22].

In this project, Raman signal enhancement, generated by an electric field propagating along the metal electrolyte interface, is selected. Silver film is employed as metal film, while zinc oxide film as an electrolyte film. As a wide band gap semiconductor nano material, ZnO has a number of excellent properties, such as high-efficiency photocatalytic performance, thermoelectric, and piezoelectric effects. In addition, cylindrical nano ZnO has a gain effect on light due to its material and morphology characteristics. Under light irradiation, the laser can be emitted through the resonant cavity mode, leading to an optical waveguide effect. In this paper, an optimal Raman enhancement method is proposed by comparing the influence of ZnO films prepared under different pH conditions on the Raman effect and the actually calculated enhancement factors. The influence of the rough substrate on the Raman effect is expressed by the difference of the hydroxide content in the nanostructure of ZnO.
2. Experimental Methods

Zinc oxide was prepared by the hydrothermal chemical deposition (HCD) method, whereas the physical vapour deposition method was utilised to prepare precious metal silver. After the preparation of the Si substrate, firstly, according to the HCD method, ZnO thin films were prepared using solutions of different pH for the subsequent growth of Ag nanoarrays. Four sets of samples were prepared for each of the four pH levels for subsequent testing. Ag nanoarrays were grown in the completed two groups of samples using 99.999% Ag. In this experiment, electron beam evaporation was used and ion source assisted deposition was used. In order to achieve the purpose of preparing the Ag nanoarray, according to the Raman electromagnetic principle, the Raman enhancement effect on the surface of the substrate was improved.

2.1. Materials Choosing and Substrate Preparation

For the evaporation of metal film, gold, silver, and copper were chosen, which were then tested by the evaporation method and sputtering method, respectively. The growth impact of the Ag nano column is found to be the best through comparison. The resistivity of silver is 14.7, which is smaller than that of gold, 26.55, and that of copper, 16.73. The electric field formed by silver nanoarrays is stronger than the other two metals. Therefore, the Raman enhancement effect is also superior to both. Moreover, the metal film prepared by the sputtering method has a small porosity, which is not conducive to the enhancement of the Raman signal, hence the silver nanoarray is finally prepared by evaporation [23,24].

2.2. Hydrothermal Chemical Deposition

Hydrothermal chemical deposition (HCD) growth refers to the crystal growth method that evaporates and escapes the water in the solvent in order to make the solution in a supersaturated state, so that the crystal growth has sufficient driving force [25,26]. The advantage of HCD is that it can produce films with complete grain development, small particle size, uniform distribution, as well as light particle agglomeration. The problems of grain growth, tangent formation, and impurity introduction during the preparation of ZnO thin films are avoided. Although the ZnO film, prepared by electron beam evaporation method, has good uniformity, it is difficult to form an island-like structure with a rough surface. Due to the plating method of PVD technology, the resulting films are all anisotropic, so the microstructure of the film itself is affected to a certain extent. Another sputtering method of evaporating ZnO thin film easily makes the thin film in a state of metallisation or peroxidation, which makes the composition of the thin film different and loses research significance. The ion source bombardment will also have a certain influence on the formation of rough island-like structures. It is also difficult to play a role in the subsequent preparation of inclined angle silver nanoarrays. Therefore, the most suitable HCD method is selected to prepare the film.

A layer of ZnO was first plated on the Si substrate (Nexteck Advanced Materials, Wenlock Road, London, UK), and ammonia was added to the zinc nitrate hexahydrate in order to adjust the pH. The sample was heated to 90 degrees Celsius in a reaction bath for 1 h, 2 h, 4 h, and 6 h. Finally, a layer of chromium and a layer of silver is plated on the sample. Since the surface structure of zinc oxide is an island structure, silver nanorod arrays are generated due to the grating effect (smooth surfaces reflect light better) during silver plating. Inter-band transitions are difficult to achieve because the energy gaps of d electrons and s electrons of group IB metals are relatively large compared to those of transition metals. As long as the appropriate wavelength of the excitation light is selected for it, the energy of the absorbed light can be prevented from being converted into heat due to the occurrence of inter-band transitions, thereby tending to realise an efficient SPR scattering process [27]. The Si substrate was first cut into several pieces and cleaned with the ultrasonic cleaner. These samples were then deposited in a DC sputtering deposition machine using Zn. In this step, put 12 samples will be placed on one plate so as to obtain 72 Zn samples in one deposition. A 5.95963 g amount of zinc nitrate hexahydrate (Umicore...
Marketing Services (Shanghai) Co., Ltd., Shanghai, China) was put into a 1 L capacity bottle and deionized water was added to the tick mark with shaking. Solutions of 50 mL were put into a brown bottle, and the pH of the solution was adjusted by adding the difference of sodium hydroxide. The pH would be 8.5, 9.0, 9.5, and 10.0. In the meantime, the samples were placed into the four bottles being placed in a heater of 90 degrees. They were heated for 4 h in the heater. Lastly, these samples were cleaned with deionized water [28, 29].

2.3. E-Beam Deposition

For the evaporation of silver films, electron beam evaporation (OTFC 1350, Optorun Co., Ltd., Tokyo, Japan) is the first choice. The physical vapour deposition (PVD) system and glancing angle deposition could be controlled by the angle of silver nanostructures. Prior to starting the experiment, cleaning the machine would be the most important thing for getting an adaptable deposition; the shutter and bracket on the device were cleaned, and all the other things would be removed from the device. The two or four samples could be stuck onto a glass piece in the next step. The glass with samples would be stuck onto the glancing angle turntable. Moreover, the crystal control part could be checked which should be above 98 percent. The system of this experiment should be set to Ag-OAD-87degA. After 5 h of vacuum, the pressure would be around $4.2 \times 10^{-7}$ mbar. The screen interface would be unlocked, and electron gun would be turned on. The pot could then be moved to part 1. At the same time, the glancing angle should be moved to 0 degrees. The first layer could be finished rapidly. Next, the angle could be changed to 87°, and the pot could be moved to part 2. Starting layer 2 is the next thing that should be done. Waiting 20 min should be done after the deposition is completed before taking the samples out to measure.

2.4. Scanning Electron Microscope

The scanning electron microscope (JEOL Ltd., SEM-JSM-IT200, Tokyo, Japan) is an observation method between a transmission electron microscope and an optical microscope [30–32]. It makes use of the narrow focused high-energy electron beam for scanning samples, exciting various physical information through the interaction between the beam and the material, and collecting and amplifying RE image information in order to achieve the purpose of characterising the micro morphology of the material [33]. In this paper, the growth morphology of zinc oxide film on silicon substrate was observed by a scanning electron microscope to determine the effect of different pH values on the structure of zinc oxide film.

3. Testing and Analysis

3.1. XRD Analysis of Zinc Oxide

Diffraction of X-rays (XRD) use monochromatic X-rays as the diffraction source and it generally penetrates the solid to verify its internal structure. As a result, XRD (Siemen X-ray Diffractometer D 5000, Berlin, Germany) provides information about the material’s bulk structure. XRD is mostly based on qualitative phase analysis, but the quantitative analysis is also possible [34]. By comparing the X-ray diffraction spectrum of the sample to be tested with the X-ray diffraction spectrum of the reference material, the phase composition of the sample can be qualitatively analysed. Quantitative analysis of the phase composition of the sample can be completed by assessing, as well as calculating, the diffraction intensity data of the sample. The material composition of zinc oxide can be determined in this experiment by examining the spectral data. According to the XRD spectrum information, it can be determined whether the sample is amorphous or crystalline: the amorphous sample has a large peak, and with no fine peak structure, the crystal has rich spectral characteristics. The sample to be tested in this experiment is a crystal. The principle is that if the crystalline elements or groups are different or their structures are different, their diffraction patterns will show differences in the number of diffraction peaks, angular position, relative intensity, and diffraction peak shape (based on the Bragg equation: $2d \sin \theta = n \lambda (n = 1, 2 \ldots)$) where $\theta$ is the angle between the incoming ray (or reflected line) and the crystal plane, also
known as the grazing angle or the reflection angle. The diffraction angle refers to the angle at which the light path changes when the light is diffracted. In the X-ray diffractometer, 2θ is the diffraction angle, because 2θ is the angle that changes the direction after X-ray diffraction; d is the interplanar spacing, λ is the wavelength of the X-ray, and n is the number of reflections. The data was shown in Table 1.

Table 1. Table list of some (h, k, and l) and 2θ for ZnO samples.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>h</th>
<th>k</th>
<th>l</th>
<th>2θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>34.50</td>
</tr>
<tr>
<td>1.47</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>61.70</td>
</tr>
<tr>
<td>2.6</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>34.40</td>
</tr>
<tr>
<td>1.91</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1.18</td>
</tr>
<tr>
<td>1.62</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2.47</td>
</tr>
<tr>
<td>2.47</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>81.80</td>
</tr>
</tbody>
</table>

The XRD scanning speed is 4°/min, and the interval angle is 0.02°. The peak of pH 8.5 and pH 9.0 samples is 2θ = 34.46° and 61.70°, and the diffraction line of pH 9.5 and pH 10.0 samples is 2θ = 34.42° and 81.78°. Cu Kα radiation (λ = 1.5406 Å) was used to obtain the X-ray diffraction data. According to the Bragg equation: 2dsinθ = nλ. It is in the air, so n = 1.0. d = nλ/2sinθ. Then, we could calculate d1 = 2.60, d2 = 1.47, d3 = 2.47, d4 = 1.91, d5 = 1.62, and d6 = 1.18. The interplanar spacing and h, k, and l would be presented in Table 2.

Table 2. List of pH, FWHM, 2theta, and D (according to the Scherrer equation: D (nano crystallite size) = Kλ/β cosθ).

<table>
<thead>
<tr>
<th>pH</th>
<th>FWHM</th>
<th>2-Theta (°)</th>
<th>D (nm)</th>
<th>pH</th>
<th>FWHM</th>
<th>2-Theta (°)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 8.5</td>
<td>1.176</td>
<td>15.061</td>
<td>6.82</td>
<td>pH 9.5</td>
<td>0.201</td>
<td>34.414</td>
<td>41.409</td>
</tr>
<tr>
<td>0.226</td>
<td>34.4</td>
<td>36.827 \n 0.217</td>
<td>37.402</td>
<td>38.681 \n 0.89</td>
<td>47.741</td>
<td>9.769 \n 0.222</td>
<td>54.637</td>
</tr>
<tr>
<td>pH 9.0</td>
<td>1.1</td>
<td>14.24</td>
<td>7.284</td>
<td>pH 10.0</td>
<td>0.594</td>
<td>30.957</td>
<td>13.889</td>
</tr>
<tr>
<td>0.194</td>
<td>34.434</td>
<td>42.905 \n 0.128</td>
<td>61.659</td>
<td>72.336 \n 0.219</td>
<td>69.107</td>
<td>44.08 \n 0.321</td>
<td>81.729</td>
</tr>
<tr>
<td>0.485</td>
<td>28.923</td>
<td>16.93 \n 0.131</td>
<td>30.968</td>
<td>62.978 \n 0.314</td>
<td>31.681</td>
<td>26.32</td>
<td></td>
</tr>
</tbody>
</table>

| pH 9.5 | 0.294 | 81.74 | 35.762 |
| 0.286 | 98.318 | 42.509 |
Figure 1 shows that when the pH rises, more ZnO peaks appear. However, for 4 h of HCD ZnO oxide, it will be the clearest one. Compared with the references of the XRD samples, it could show seven kinds of peaks in the figures: one for Si, six for ZnO. The Si peak is about 69° and the intensity of those peaks are around 25,000–30,000. When the pH for HCD changes, the crystal type changes as well. The 1 h, 2 h, 4 h, and 6 h data appeared amorphous, however, 4 h could obtain the crystal. This suggests that there is a positive relationship between the generation of crystals and the time of hydrothermal evaporation in the first part, whereas there is a reverse relationship in the latter part. The best value can be obtained through a large number of experimental tests, which are the 4 h results of this experiment [35]. In future work, it will be controlled for about 4 h for HCD so that it can obtain crystals in the results.

The Scherrer equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \] (1)

was developed in 1918 in order to calculate the nano crystallite size \( D \) by XRD radiation of wavelength \( \lambda \) (nm) from measuring the full width at half maximum of the diffraction line beta in radian located at any 2 \( \theta \) in the pattern. The shape factor of \( K \) can be 0.62–2.08 and is usually taken as about 0.89. However, if all of the peaks of a pattern give a similar value of \( D \), then beta cos theta must be identical. This means that for a typical 5 nm crystallite size and lambda CuKa1 = 0.15405 nm, the diffraction line at 2 \( \theta \) = 170° must be more than ten times wide with respect to the peak at 2 \( \theta \) = 10°, which is never observed. Calculating the average crystallite size by the Debye Scherrer equation requires FWHM. The FWHM was calculated with the help of the origin program. The XRD mode extended by re-adjusting the pattern around the peaks required for any FWHM calculation. The maximum intensity

![Figure 1. ZnO XRD data for different HCD time. (a): ZnO (made by 1 h HCD) XRD data. (b): ZnO (made by 2 h HCD) XRD data. (c): ZnO (made by 4 h HCD) XRD data. (d): ZnO (made by 6 h HCD) XRD data.](image)
of the peak was then measured by using a screen reader tool. The name $\beta$ is half the peak width of the peak width, the X1 and X2 values of the peak at half of the maximum intensity were calculated, with the difference between X1 and X2 giving the FWHM of the peak. $\beta$ is related to grain size, as we saw in the standard JCPDS data. It is a pattern of bulk material (extremely large size), with merely one line visible at the peak position, indicating that the FWHM of the JCPDS data peak is the minimum or close to zero. However, as the grain size decreases, the FWHM increases, which makes it clear that the FWHM is inversely proportional to the average crystallite size of the material. A summary of the XRD data is given in Table 2 [36].

With the increase in pH, the nano crystallite size ($D$) increases first and then decreases. That is, when the pH is 9.0, $D$ is the largest. The value of FWHM is first reduced and then increased, while the size did not change with the changes of 2 theta.

3.2. Surface Morphology

The ZnO films prepared at different pH values were tested using a Scanning electron microscope (JEOL Ltd., SEM-JSM-IT200, Tokyo, Japan). The SEM pattern is shown in the figure.

Figure 2 depicts that: as the pH increases, the deposition rate increases. The nanorods of the sample of pH 8.5 were thicker and shorter, whereas the nanorods of the sample of pH 9.5 were thin and long. In comparison, the homogeneity of the sample at pH 9.5 is also the best. On the graph, the zinc oxide nanowires could be seen. From the top view of zinc oxide, the film is uniform. The nanostructures were shown in the figures. Based on the HCD work we did before, we obtained adaptable ZnO nanostructures. They are uniform and have island structures, which allow us to obtain a good structure for the deposition of silver and hence make a good silver structure.

Table 3 were drawn from the data obtained from the SEM figures. With the increase in pH value, the thickness of the prepared ZnO nanofilm gradually increased, and the diameter of the ZnO nanopillar also gradually increased. With the increase in pH, the film thickness changes almost linearly.

![Figure 2](image_url)
Figure 2. (a). SEM images of ZnO thin films prepared by hydrothermal evaporation on silicon substrates at pH 8.0. (b). SEM images of ZnO thin films prepared by hydrothermal evaporation on silicon substrates at pH 9.0. (c). SEM images of ZnO thin films prepared by hydrothermal evaporation on silicon substrates at pH 9.5. (d). SEM images of ZnO thin films prepared by hydrothermal evaporation on silicon substrates at pH 10.0.
Table 3. Enhancement calculation for the different noble metal substrate.

<table>
<thead>
<tr>
<th>pH</th>
<th>Thickness (nm)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>374</td>
<td>72.8</td>
</tr>
<tr>
<td>9.0</td>
<td>522</td>
<td>63.9</td>
</tr>
<tr>
<td>9.5</td>
<td>950</td>
<td>78.7</td>
</tr>
<tr>
<td>10.0</td>
<td>1350</td>
<td>130.3</td>
</tr>
</tbody>
</table>

3.3. Raman Scattering Spectroscopy and Raman Mapping

The Thermo Scientific™ DXR™ 3 Raman spectrometer is used. The laser wavelength is 532 nm and the laser power is 100 MW. The integration time is set to 0.1 s and the resolution is set to 0.5. Objective magnification is 50×, and the slit size is 10 mm. Raman spectroscopy is a sensitive and effective technique used to detect the atomic vibrational modes in different kinds of materials [37]. Raman spectra were measured on ZnO, AgNPs/ZnO/Si, AuNPs/ZnO/Si, and CuNPs/ZnO/Si structures, and the results are shown in Figure 3.

![Raman spectra of simple ZnO, AgNPs/ZnO/Si, AuNPs/ZnO/Si, and CuNPs/ZnO/Si structures.](image)

It can be seen from the figure that the Raman effect of the ZnO Raman substrate based on silver nanoarrays is stronger. SERS substrate activity was measured by the surface enhancement factor (EF) [38]. EF refers to the ratio between the SERS signal of the target molecule on the substrate and the conventional Raman signal of these molecules when the number of molecules is the same, which can be expressed as

$$EF = \frac{I_{surf}}{I_{bulk}} \times \frac{N_{bulk}}{N_{surf}}$$

According to the formula calculation, the calculation results of the surface enhancement factor are shown in Table 4.

Table 4. Enhancement calculation for the different noble metal substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>611 cm⁻¹</th>
<th>Enhancement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>42.214</td>
<td>1</td>
</tr>
<tr>
<td>CuNPs/ZnO/Si</td>
<td>8642.916</td>
<td>$2.04 \times 10^2$</td>
</tr>
<tr>
<td>AuNPs/ZnO/Si</td>
<td>29,342.443</td>
<td>$6.95 \times 10^2$</td>
</tr>
<tr>
<td>AgNPs/ZnO/Si</td>
<td>592,145.872</td>
<td>$1.40 \times 10^4$</td>
</tr>
</tbody>
</table>
The nanowire in this picture was chosen for measure. The more the number of measurements points you select, the wider the range of measurements, and the more accurate the measurement is. These points were selected to represent the Raman image of the sample to be tested (Figure 4).

![Figure 4. 1606 cm\(^{-1}\) line Raman map, ZnO (pH9)/15 nm Cr/450 nm Ag nominal thickness (87GLAD).](image)

The figure’s majority of the parts are green, although some of parts are blue and yellow. It confirms that the surface of the sample is not very uniform. Some conditions in this experiment should be adjusted to make our samples more uniform.

Figure 4 was shown pH 9.0 Raman map data. From the Figure 5, the nanowire is smooth, but not very uniform, so we can try other methods to make it better in future work. The enhancement Raman shift position is 1582 cm\(^{-1}\).

![Figure 5. Raman spectroscopy on the position (micrometres) = 8924 \(\mu\)m, point #211.](image)

It is obvious that the nanostructure is clearer than the pH 9.0 samples. The surface uniformity of the Raman imaging map substantially improved compared to previous samples. The majority of the part is green, while a few parts are yellow and blue. This demonstrates that the homogeneity of the sample at pH 9.0 is higher in contrast to the homogeneity of the sample at pH 10.0. In future experiments, adjusting the pH appropriately to maintain it near pH 9.0 could enhance its uniformity.

The samples are pH 10.0 on the Raman map data, and according to the demonstration of Figures 4–7, the uniformity of the film gradually deteriorated as the pH increased after pH exceeded 9. There are bumps on the surface of the film, which affect the quality of
the overall film. Raman-enhanced signals are also weakening [38]. In these figures, the nanostructure is better than the pH 9.0 samples, although it is still not very perfect. In future work, we can try using sodium hydroxide to control the pH, as it might work better in uniform parts. It would be an enhancement for the samples using the peak area divided by the concentration of bisphenol A ethoxylate (BPE). Furthermore, the concentration is \(10^{-6}\). As a result of this, the enhancement is shown in Table 4.

![Figure 6. 1606 cm\(^{-1}\) line Raman map, ZnO (pH10)/15 nm Cr/450 nm Ag nominal thickness (87GLAD).](image)

Table 5 shows the EF for pH 9 samples and pH 10 samples. The EF of pH 9 (best- HQ) arrives at \(2.07 \times 10^4\). For Raman spectroscopy, this is quite a high enhancement. As for the EF pH 10, it would be a low enhancement. Hence, the influence of pH in the HCD for ZnO with silver is critical for enhancement. In XRD data could reveal the ZnO crystal at pH 9, too. So, the complete ZnO crystal is an important thing in this research. Furthermore, it should be controlled at pH 9 in this kind of experiment to obtain a good nanowire for Ag nanorod growth. In this project, we investigated which pH of ammonia is ideal for making good ZnO nanowires using HCD as a substrate of silver SERS substrates. In the XRD curve, a single diffraction peak (002) appeared in the sample with a ZnO preparation heating time of 4 h and a pH of 9. In the SEM test, the PH9 sample is also a uniform nanoarray that can produce the best hexagonal wurtzite structure. It can be seen that the growth structure,
orientation and growth direction of ZnO nanoarrays are important factors affecting the Raman enhancement effect. The best surface-enhanced Raman scattering substrate can be prepared by ZnO nanoarrays with high orientation and appropriate porosity.

Table 5. Enhancement calculation for the Raman enhancement substrate at different pH.

<table>
<thead>
<tr>
<th></th>
<th>1595 cm⁻¹</th>
<th>[BPE]</th>
<th>Enhancement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPE on Ag</td>
<td>77,199</td>
<td>1.0 × 10⁻⁴</td>
<td>1</td>
</tr>
<tr>
<td>pH 9 (best-HQ)</td>
<td>15,943.736</td>
<td>1.0 × 10⁻⁶</td>
<td>2.07 × 10⁴</td>
</tr>
<tr>
<td>pH 9 (100)</td>
<td>14,614.031</td>
<td>1.0 × 10⁻⁶</td>
<td>1.89 × 10⁴</td>
</tr>
<tr>
<td>pH 9 (100) variance</td>
<td>1421.111</td>
<td>1.0 × 10⁻⁶</td>
<td>1.84 × 10³</td>
</tr>
<tr>
<td>pH 10</td>
<td>686.772</td>
<td>1.0 × 10⁻⁶</td>
<td>8.90 × 10²</td>
</tr>
<tr>
<td>pH 10</td>
<td>3712.618</td>
<td>1.0 × 10⁻⁶</td>
<td>4.81 × 10³</td>
</tr>
<tr>
<td>pH 10</td>
<td>1761.464</td>
<td>1.0 × 10⁻⁶</td>
<td>2.28 × 10³</td>
</tr>
<tr>
<td>pH 10</td>
<td>694.645</td>
<td>1.0 × 10⁻⁶</td>
<td>9.00 × 10²</td>
</tr>
</tbody>
</table>

Figure 8 was shown to express the spectra for different Ph. Comparing the spectral response spectra, the differences of zinc oxide films prepared with different pH levels can also be observed, so that the magnitude of the Raman enhancement effect can be judged according to its characteristics.

![Spectroscopy](image_url)

Figure 8. Spectral response spectra of ZnO films prepared at different pH values and only Ag nanoarrays.

For the preparation of ZnO nanoarrays, the method of hydrothermal evaporation was adopted in this paper, and the height and morphology of the nanoarrays were controlled by adjusting the pH. Compared with other advanced deposition methods, it not only effectively improves its enhancement factor, but also realises the control of strength to a certain extent. It has potential applications in medical, drug delivery, photothermal heat generation, photodetection, light harvesting, photocatalysis, agricultural and anti-drug fields. Its discrimination of different materials can be tuned by the way it controls the strength of reinforcement. However, to obtain nanorods with higher thicknesses, other deposition methods need to be tried. For example, the reactive deposition method realized by the cathode sputtering method uses a metal Zn target, which is filled with a mixed gas of argon and oxygen to make reactive sputtering, and its thickness is controlled by an optical film thickness control system [39].
4. Summary

ZnO thin films were prepared on silicon substrates by hydrothermal synthesis, and then silver nanoarrays were evaporated on ZnO thin films by glancing angle deposition, which enhanced the surface Raman scattering signal. Controlling the pH of ammonia is crucial for making an adaptable nano ZnO by HCD. The enhancement effects of ZnO substrates prepared at different pH values with surface Raman scattering were measured and compared using SEM, Raman spectrometer, XRD, along with other test instruments. Compared to the SEM result and XRD result, we can observe a good ZnO nanostructure and also know the pH 9.5 and pH 10.0 samples are successful. The (002) ZnO peak was shown in the XRD spectroscopy. It confirms that the ZnO nanostructure was deposited successfully.

With the increase in pH value of zinc nitrate solution, the proportion of hydroxyl in the solution gradually increases, and the excess OH bond will combine with the cation. When the oxygen content reaches 10 sccm, the generated zinc oxide has sufficient oxygen content, and the zinc oxide enters the peroxygen state. When the number of OH bonds reach a certain amount, so that the oxygenation amount reaches 15 sccm, the proportion of ZnO oxygen ions gradually decreases. The required zinc oxide with (002) ZnO hexagonal prism structure is in a state of moderate OH radical content; that is, when the pH value is about 9.0 to 9.5. With the increase of reaction time, the crystal column arrangement of ZnO gradually changes from sparse to compact. Too sparse ZnO is difficult to arrange neatly, resulting in poor uniformity of ZnO, which limits the arrangement of Ag nano columns to a certain extent. Too dense an arrangement will gradually reduce the porosity and affect the excitation of the surface-enhanced Raman scattering effect. Therefore, 4 h of HCD is a moderate reaction time. Subsequent research will select the atomic layer deposition method from the preparation of ZnO thin films to try to make the surface more uniform and to produce island-like structures. In addition, improvements will be made in the deposition method of noble metal materials to increase the porosity of the nanoarrays.

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References

2. Fleischmann, M.; Hendra, P.; McQuillan, A. Raman spectra of pyridine adsorbed at a silver electrode. Chem. Phys. Lett. 1974, 26, 163–166. [CrossRef]
22. Liang, X.; Liang, B.; Pan, Z.; Lang, X.; Zhang, Y.; Wang, G.; Yin, P.; Guo, L. Tuning plasmonic and chemical enhancement for SERS detection on graphene-based Au hybrids. Nanoscale 2015, 7, 20188–20196. [CrossRef]
29. He, Y.; Zhao, Y. Advanced multi-component nanostructures designed by dynamic shadowing growth. Nanoscale 2011, 3, 2361–2375. [CrossRef]
