Trace detection of herbicides by SERS technique, using SERS-active substrates fabricated from different silver nanostructures deposited on silicon

Tran Cao Dao¹, Truc Quynh Ngan Luong¹, Tuan Anh Cao², Ngoc Hai Nguyen¹, Ngoc Minh Kieu¹, Thi Thuy Luong¹ and Van Vu Le³

¹ Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
² Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan, Ba Dinh, Hanoi, Vietnam
³ Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

E-mail: dtcao@ims.vast.ac.vn

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Abstract
In this report we present the initial results of the use of different silver nanostructures deposited on silicon for trace detection of paraquat (a commonly used herbicide) using the surface-enhanced Raman scattering (SERS) effect. More specifically, the SERS-active substrates were fabricated from silver nanoparticles (AgNPs) deposited onto the flat surface of a silicon wafer (AgNPs@Si substrate), as well as on the surface of an obliquely aligned silicon nanowire (SiNW) array (AgNPs@SiNWs substrate), and from silver nanodendrites (AgNDs) deposited onto the flat surface of a silicon wafer (AgNDs@Si substrate). Results showed that with the change of the structure of the SERS-active substrate, higher levels of SERS enhancement have been achieved. Specifically, with the fabricated AgNDs@Si substrate, paraquat concentration as low as 1 ppm can be detected.

Keywords: surface-enhanced Raman scattering SERS, SERS-active substrates, Ag nanoparticles, Ag nanodendrites, silicon nanowires

Classification number: 5.08

1. Introduction

It is well known that Raman scattering is a valuable tool for identification of chemical and biological samples, as well as for the elucidation of molecular structure. This is due to the origin of appearance of this type of scattering. In the Raman effect, incident light is inelastically scattered from a sample and shifted in frequency by the energy of its characteristic molecular vibrations. Despite such advantages, Raman scattering suffers the disadvantage of extremely poor efficiency. It has been estimated that, on average, of 10⁶–10⁸ photons that fall into the material, only one photon has been Raman scattered [1]. Thus the intensity of the Raman signal measured is usually very weak.

A great turning point occurred in 1977, when it was first discovered that the presence of a suitable metal surface close to the analyte molecules will make the Raman signal increase 10³–10⁶ times [2, 3]. The effect was later named as surface-enhanced Raman scattering (SERS) and thus began the era of SERS. Within this phenomenon, molecules adsorbed onto metal surface under certain conditions exhibit an anomalously large interaction cross-section for the Raman effect. With time, SERS has developed into an analytical technique to detect the presence of trace amounts of organic and biological molecules. In some cases, SERS can even detect single molecules [4, 5].

As the name ‘surface-enhanced Raman scattering’ indicates, the amplification of the Raman signal depends strongly
on the nature and characteristics of the metal surface on which the analyte molecules are adsorbed. It was found that only a few ‘free-electron-like’ metals, mainly Ag, Au and Cu could provide a large SERS effect. Among them silver has been demonstrated as the most suitable material for SERS studies. Next, it was also observed that SERS activity strongly depends on the surface roughness, the smooth surface is not active for the enhancement. Instead of a roughened surface, one can also use an assembly of metal particles. But in that case, generally the particle size required in order to have the maximum Raman scattering enhancement ranges from several tens to hundreds of nanometers [6]. Metal surface or assembly of metal nanoparticles that is used in order to amplify the Raman scattering signal of the analyte molecules when they are adsorbed onto it is commonly known as SERS-active substrate. Since the discovery of SERS, a key problem in an analytical application of SERS is to develop stable and reproducible SERS-active substrates that can provide as large as possible enhancement factor. To find out the requirements for a SERS-active substrate, first we have to know how the Raman signal was enhanced in the SERS phenomenon.

At present, it is widely accepted that there are two mechanisms to describe the overall SERS effect: the electromagnetic (EM) effect and the chemical effect. After decades of debate, it is now generally agreed that the dominant contributor to most SERS processes is the EM mechanism [7]. Specifically, under appropriate circumstances, SERS enhancements as large as $10^{14}$ can be achieved [8], in which at least 8–10 orders of magnitude can arise from the EM effect, while the enhancement factor due to the chemical effect is only $10^3$–$10^7$ times [9, 10]. In brief, the EM mechanism can be explained as follows. Under the excitation of an incident laser light, free electrons on the metal surface are excited to a collective oscillation against the metal cores. When this collective oscillation (which was named plasmon) is in resonance with the frequency of the incident light, the localized surface plasmon resonance (LSPR) occurs [11, 12]. On a rough metal surface, where the analyte molecules are adsorbed, the LSPR would lead to a local EM field enhancement and result in the enhancement of Raman signal of the analyte molecules [13, 14]. The strength of LSPR on the metal surface is determined by the frequency of excitation light and the surface roughness of substrates. By controlling the shape (surface morphology), size, and the spacing between nanoparticles, one can tune the LSPR to obtain the optimized SERS signal from the metal nanostructures at a desired wavelength [15, 16]. Among those factors, surface morphology and inter–particle spacing are particularly important. Firstly, it has been found that the close distance between the nanoparticles (in the region of a few nanometers) can enormously enhance the Raman signals of analyte molecules [17]. Secondly, due to the surface plasmon polarization (SPP) of the high curvature surface of the nanostructures such as tips and sharp edges, strong SERS enhancement is established according to the experimental and simulation results [18, 19]. Therefore, instead of using nanoparticles (with spherical or nearly spherical shape) in the SERS-active substrate, in recent times there was a strong shift to using hierarchical nanostructures with complex shapes, such as dendrite-like, flower-like or urchin-like nanostructures [20–26]. The regions of highly enhanced local EM field are called ‘SERS hot spots’. The presentation above shows that the gap between the nanoparticles, the tip, the sharp protrusions of the nanostructures...are the main hot spots.

In the early days of SERS, roughened at the nanoscale surfaces have been used as SERS-active substrates. Then people began moving to use the assemblies of metal nanoparticles or nanostructures. Currently two main types of such assemblies are being used as SERS-active substrates: a collection of metal nanoparticles/nanostructures in a colloidal solution (colloidal substrate) and an assembly of metal nanoparticles/nanostructures on a solid-state surface (solid substrate). However, the colloidal substrates created by wet-chemical methods are naturally unstable because of the uncontrollable aggregation, as well as the constant movement of nanoparticles, and the precipitation of particles in solution may lead to the loss of the SERS activities of the colloids. Hence, as an ideal choice for such a problem, fabricating metal nanoparticles or nanostructures on a solid matrix as a detection device not only intrinsically provides more reproducible and stable SERS measurements but also facilitates the migration of SERS detection from the laboratory to in-field applications [27].

In this paper we present the preliminary results related to the fabrication of solid SERS-active substrates with increasing SERS activity. These SERS-active substrates were fabricated by depositing the silver nanoparticles (AgNPs) or nanodendrites (AgNDs) on silicon surface. Silicon was chosen primarily because it has the ability to allow a relatively thick layer of AgNPs/AgNDs associated with its surface. In turn, this could have happened because one can perform the silver deposition process simultaneously with silicon etching. For the SERS-active substrate category with AgNPs deposited on silicon surface, two subcategories were produced. The first subcategory includes AgNPs deposited onto the flat surface of a silicon wafer, and the second subcategory includes AgNPs deposited onto the surface of silicon nanowires that belongs to an aligned silicon nanowire (SiNW) array. From now on, the first subcategory of substrates mentioned above will be referred to as AgNPs@Si, while the second one will be known as AgNPs@SiNWs. By using SiNW array, the effective surface area of silicon is increased very sharply, so the number of AgNPs deposited on the silicon surface is also increased greatly. Moreover, when the molecules of the analyte are introduced in a SERS-active substrate of the AgNPs@SiNWs type, they are surrounded by the AgNPs on many directions, like in a colloidal substrate. Therefore we can expect that SERS magnification will increase significantly compared to the case of AgNPs@Si. Concerning the case of silver nanodendrites deposited on the flat surface of a silicon wafer (which hereinafter will be referred to as AgNDs@Si), we can say that because here there are many tips and sharp edges, as well as very close distance between the silver nanostructures, the number of the hot spots is increasing drastically, with the result that we can also expect a great SERS enhancement.
Our purpose in this study is the engineering of SERS substrates with high SERS enhancement to detect trace amounts of herbicides. Therefore for testing the SERS activity of the above mentioned substrates, the molecules of paraquat were used as probes. Paraquat (PQ) is a fast-acting and non-selective herbicide widely used in Vietnam and in many other countries for chemical weed control [28]. PQ is known to be highly toxic for humans; especially it has toxic effects on human heart, liver, and brain tissue. PQ exposure has a high mortality rate attributed to a lack of effective treatments [29, 30]. Contributing to the severity of PQ toxicity is its high solubility in water [31].

2. Experimental

The AgNPs@Si substrate is facilely synthesized via in situ growth of AgNPs on silicon wafers by an established HF-etching assisted chemical reduction method, i.e. Ag ions are reduced by Si-H bonds covered on surface of H-terminated silicon wafers. The synthesis was carried out in a similar way to what has been shown in [32]. Briefly, the cleaned silicon wafer was immersed in 5% HF solution for 30 min to achieve H-terminated silicon wafer. The silicon wafer covered by Si-H bonds was then immediately placed into a freshly prepared reduction solution containing silver nitrate (AgNO₃) with a concentration of 0.1 mM, accompanied by slight stirring for 3 min, achieving the AgNPs@Si structure.

The substrates of the AgNPs@SiNWs type have been fabricated in a way similar to what was shown in [33]. More specifically, from an initial Si wafer with (111) orientation, the obliquely aligned SiNW arrays were fabricated by the metal-assisted chemical etching (MACE) method. Then the AgNPs were deposited onto the surface of SiNWs. This deposition was conducted in a similar manner as when creating AgNPs on the silicon wafer surface. It is worth noting that obliquely aligned SiNW arrays, rather than vertically aligned SiNW arrays, were used. The reason of this is to have the AgNPs evenly distributed over the entire length of the nanowires, rather than AgNPs concentrated only near the tip of the nanowires, as was explained in [33].

The SERS-active AgNDs@Si substrate has been manufactured in a similar way as the AgNPs@Si substrate above, except the AgNO₃ concentration in the reduction solution was increased to 20 mM (i.e. increased 200 times). Fabrication time can vary between 3 to 15 min, depending on desired thickness of the AgNDs layer.

After fabrication and thorough washing, the SERS substrates of all types were stored in deionised water for further use. The structure and morphology of representative SERS-active substrates were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), using, respectively, a S-4800 Field Emission Scanning Electron Microscope (Hitachi, Japan) and an JEM 1010 Transmission Electron Microscope (JEOL, Japan).

As mentioned above, methyl viologen dichloride hydrate (paraquat) molecules were used as test molecules in Raman spectroscopy. The paraquat molecules were deposited by dripping 50 μl of aqueous paraquat solution with different concentrations onto the substrate surface. The spreading area is ∼1 x 1 cm². After paraquat dripping, samples were let stand in air at room temperature until dry. Only then Raman spectrometry was performed. Raman spectra were recorded with a Jobin-Yvon LabRam Raman microscope with input laser light of 632.8 nm wavelength.

3. Results and discussion

The results of fabrication of the AgNPs@Si, AgNPs@SiNWs and AgNDs@Si structures are illustrated in figures 1, 2 and 3, respectively. Figure 1 shows that the fabricated AgNPs are of the kind with almost circular shape, with relatively uniform size of 30–50 nm, and evenly distributed over the surface of the silicon wafer. It should be noted that not all of these AgNPs are located on a flat silicon surface, but perhaps some of them were sunk into the silicon, as silicon etching has occurred simultaneously with the AgNPs deposition.

From figure 2(a) we can see that the obliquely aligned SiNWs are uniformly distributed over the entire surface of the substrate and most of them are oblique at an angle of 60° to
this surface. The length of most of the SiNWs is $\sim 7\ \mu m$. The TEM image of a representative single silicon nanowire after AgNPs coating is shown in figure 2(b). From this image, we can estimate that the diameter of SiNWs is in the range of 100–200 nm, in addition, we can also see the AgNPs are attached to the surface of the SiNWs as small black dots (with diameter in the range of 20–40 nm) after silver deposition. The density of AgNPs is relatively high and AgNPs are distributed fairly evenly over the entire surface of the SiNW fibres.

Typical SEM images of the as-synthesized AgNDs are shown in figure 3. The high-magnification image in figure 3(a) shows that an Ag dendrite consists of a long main trunk with short side branches. The diameter of the trunk is around a few hundred nm, and its length is up to tens of micrometers. The low-magnification image in figure 3(b) shows a large number of Ag dendrites with an almost uniform distribution. The Ag dendrites are very reproducible with apparent self-similarity. We would like to reiterate that according to what we have gained, AgNDs were obtained instead of AgNPs, when the AgNO$_3$ concentration in the reduction solution is significantly increased. This is understandable if we use the diffusion-limited aggregation (DLA) model to explain the growth mechanism of Ag dendritic structure [34]. Firstly, AgNPs hit and stick with each other, thus forming initial aggregates of AgNPs. Then, more and more free nanoparticles will diffuse toward the aggregates to form larger aggregates by the continuous hitting and sticking processes. At first, the backbones of the dendrites are formed. As the reaction proceeds, the growth is mainly driven by the decreasing surface energy, and the growth of the nanostructure prefers to occur at tips and stems of the branches. Thus the dendritic Ag nanostructures are formed by anisotropic growth of the aggregates.
SERS spectra of paraquat aqueous solutions with different paraquat concentrations dripped on the AgNPs@Si, AgNPs@SiNWs and AgNDs@Si substrates are shown in figures 4, 5 and 6, respectively. In accordance with the data of [35], all well-separated and strong peaks in these figures are the Raman peaks of the PQ molecule. From figure 4 we can see that the minimum concentration of paraquat that the AgNPs@Si SERS-active substrate can detect is ∼100 ppm. Meanwhile, this limit is ∼10 ppm for the AgNPs@SiNWs substrate (figure 5), and ∼1 ppm for the AgNDs@Si substrates (figure 6). This means that by changing the structure of SERS-active substrates we have increased 100 times the detection limit for paraquat. This also demonstrates that the surface morphology of the silver nanostructures play a crucial role in determining the magnitude of the SERS enhancement.

4. Conclusions

In conclusion, different SERS-active substrates fabricated from silver nanostructures deposited on silicon surface were fabricated, with the aim of finding out which kind of substrates will have greater SERS enhancement, enough to detect trace amounts of the paraquat, a commonly used herbicide. The results showed that among the three types of SERS-active substrates which have been manufactured—AgNPs@Si, AgNPs@SiNWs and AgNDs@Si—the AgNDs@Si type has the largest Raman signal amplification. With this best SERS-active substrate type, we have detected paraquat concentrations as small as 1 ppm, while with the AgNPs@Si substrate, the lowest concentration of paraquat which can be detected, is 100 ppm. This suggests that the surface morphology of the silver nanostructures play a very important role in determining the magnitude of the SERS enhancement.

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