

FABRICATION OF SILVER NANOSTRUCTURES IN THE FORM OF PARTICLES, DENDRITES AND FLOWERS ON SILICON FOR USE IN SERS SUBSTRATES

DAO TRAN CAO^{1,2†}, LUONG TRUC QUYNH NGAN^{1,2}, CAO TUAN ANH³
AND KIEU NGOC MINH⁴

¹*Institute of Materials Science, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet, Hanoi, Vietnam*

²*Graduate University of Science and Technology, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet, Hanoi, Vietnam*

³*Tantrao University, Trung Mon, Yen Son, Tuyen Quang, Vietnam*

⁴*Center for Vocational Education - Continuing Education of Phuc Yen city,
Ngo Gia Tu, Hung Vuong, Phuc Yen, Vinh Phuc, Vietnam*

E-mail: [†]dtcao@ims.vast.ac.vn

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Abstract. *Surface Enhanced Raman Scattering (SERS) is a technique that is increasingly being used to detect trace amounts of various types of molecules, especially organic and biological molecules. The SERS effect is available mainly due to the SERS substrate - a noble metal surface that is rough at the nano level or a set of noble metal nanoparticles in a certain arrangement. Such a SERS substrate acts as an analyte Raman signal amplifier and can provide amplification up to millions of times and even more. The amplification coefficient of the SERS substrate is determined mainly by the number of 'hot spots' it contains as well as the 'hotness' of these spots. In turn, a 'hot spot' is a certain space around the tips or a nanogap between particles, where the local electromagnetic field is intensely enhanced, while the 'hotness' is determined by the sharpness of the tips (the sharper the hotter) and tightness of the gaps (the narrower the hotter). This report presents an overview of the research results of fabricating a type of SERS substrate with a high enhancement factor, which is the SERS substrate made from silver nanostructures coated on the silicon surface. With the aim of increasing the number of 'hot spots' and their quality, as well as ensuring uniformity and reproducibility of the SERS substrate, silver nanostructures have been fabricated in various forms, such as nanoparticles, nanodendrites and nanoflowers.*

In addition, the report also mentions the use of the above silver nanostructures as SERS substrates to detect trace amounts of some pesticides and other toxic agents such as paraquat, pyridaben, thiram, cyanide...

Keywords: SERS, silver, silicon, nanoparticles, nanodendrites, nanoflowers.

Classification numbers: 52.38.Bv; 61.46.Df; 68.70.+w.

I. INTRODUCTION

Raman spectroscopy is a technique commonly used to identify molecules based on their vibrating energy levels [1, 2]. In Raman scattering, photons are scattered inelastically, which means that they either lose or gain an amount of energy exactly equal to the vibrational energy of the molecule of the material being examined, thereby creating Raman spectral shift bands that are specific to each type of molecule. However, normally Raman scattering has a very low probability of occurrence. In general, for every $\sim 10^6$ - 10^8 photons that fall on the material, only one photon is Raman scattered, so the measured Raman signals are often extremely weak. From here one can see that detecting small amounts of a molecule represents a great challenge to conventional Raman spectroscopy.

An important turning point occurred in 1974, when it was first discovered that the presence of an appropriate rough metal surface would cause the analyte's Raman signal to increase to 10^3 - 10^6 times [3–5]. Thus began the era of “Surface Enhanced Raman Scattering” (SERS) as an analytical technique for trace identification of organic and biological molecules. Today, although the causes of SERS are still under discussion, it is believed that there are two main mechanisms of Raman signal enhancement, namely, enhancement of the electromagnetic field (which may cause Raman signal enhancement up to 10^{12} times) and chemical enhancement (which can boost Raman signal up to 10^2 times), i.e. thanks to SERS the total Raman signal can be maximally increased up to 10^{14} times.

To get the SERS effect, one must first have a surface made of the appropriate metal (usually a precious metal, preferably silver (Ag) or gold (Au)) and suitably rugged (preferably at the nano level). Then the molecules to be analyzed are deposited (adsorbed) onto this surface. Such a surface can also be replaced with a suitable metal nanoparticle system. The aforementioned metal nano-rough surface or the metal nanoparticle system is often called the SERS substrate. Thus, the SERS substrate is the sensor that enhances the Raman signal or the Raman signal amplifier, which plays a decisive role in how many times the Raman scattering signal of the analyte is amplified.

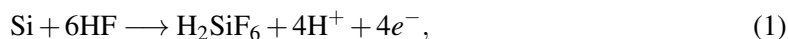
If we accept that enhancement of the electromagnetic field is the main mechanism, then a good SERS substrate must have many areas where the electric field is intensely increased. These areas are often referred to as 'hot spots' and they are usually the areas around the tips and the gaps between the particles. Note that the 'hotness' of hot spots will become higher as the tips will be sharper and the gaps will be narrower (with a width of only a few nanometers is the best). It is for the reason that dendritic and flower structures have more sharp tips than the particle structure (with particles usually having an almost spherical shape), we have moved from fabricating the SERS substrate in the form of nanoparticles to nanodendritic form and then to nanoflower form. The dendritic structure has many sharp tips, so it usually gives the best SERS enhancement factor. However this structure is usually quite large (with the length of the main stem of the structure

usually up to a few tens of micrometers) making the SERS substrate to become poor in uniformity, so we had to switch to using nanoflower structures.

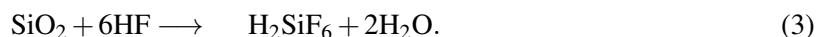
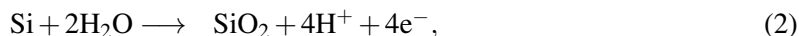
As mentioned above, the best material for SERS substrate is usually silver or gold metal. The main reason we have chosen silver over gold is that silver is ‘more analyte-friendly’ in the sense that silver is more likely to allow other substances to stick (adsorb) on its surface than gold [6]. As we know, in order to be analyzed by SERS a substance must first adhere to the surface of the SERS substrate. It is documented that under similar conditions the SERS substrates made of silver give the SERS enhancement factor of 100-1000 times higher than the SERS substrates made of gold [7, 8].

Currently two main types of SERS substrates are common, the first being SERS substrates in which metal nanoparticles or metal nanostructures are suspended in an aqueous solution, and the second is the SERS substrates in the form of an array of metal nanoparticles or nanostructures immobilized on a solid substrate. SERS substrates in the form of colloidal solutions are currently most commonly used, but they have the disadvantage of poor reproducibility due to Brown movement of nanoparticles or nanostructures in solution. Therefore, SERS substrates in solid form are becoming more and more popular.

In the following we will present the reasons why we chose silicon as the initial substrate, then deposited on it with nanoparticles or nanostructures of a metal (more specifically, silver) to produce a SERS substrate. Silicon was first chosen because it has many excellent properties, including its neutrality on the vast majority of analytes, its lack of fluorescence background in the SERS substrate [9] and its cheapness and availability. Next, if the silver nanoparticles or nanostructures are produced on silicon by the process of chemical reduction of some silver salt (e.g. silver nitrate - AgNO_3) which has been dissolved in solution, it should be noted that the silicon is also the reducing agent [10, 11]. More specifically, in this process silver and silicon form a redox pair. While silicon is oxidized to a compound that dissolves into solution and produces free electrons, silver ions (which are present in solution due to the ionization of the silver salt) take over these electrons, and thus they are reduced to elemental silver that attaches to the silicon surface in the form of nanoparticles or nanostructures. When working with silicon, hydrofluoric acid (HF) is used very often, so it is important to note that silicon can be oxidized in two ways, either through reaction with HF to produce soluble compound H_2SiF_6 and free electrons according to the equation:



or by reacting with H_2O to create SiO_2 and free electrons, then this SiO_2 reacts with HF to also produce soluble H_2SiF_6 as before, according to the equations:



Meanwhile, the silver ions are reduced to elemental silver according to the following equation:



In short, during the chemical deposition of silver on silicon, silicon itself participates in the redox reaction, so that part of its surface is etched away and thus silver will better adhere to silicon. This is a great advantage for choosing silicon as the initial substrate for silver deposition. Another reason for the silicon choice that we would like to mention is that many of the commercial

SERS substrates that are currently available on the market are gold or silver nanostructures coated on silicon. More specifically, that is the case of the commercial SERS substrates like Renishaw's Klarite, Silmeco's SERStrate, Nanova's Q-SERS, and so on [12–14].

In this report, we present an overview of fabrication results of SERS substrates with high enhancement factor made from silver nanostructures coated on silicon surface. With the aim of increasing the number of 'hot spots' and their 'hotness', as well as ensuring uniformity and reproducibility of the SERS substrate, silver nanostructures have been fabricated in various forms, such as nanoparticles, nanodendrites and nanoflowers. In addition, the report also mentions the use of the above silver nanostructures as SERS substrates to detect trace amounts of pyridaben. Pyridaben (molecular formula $C_{19}H_{25}ClN_2OS$) is an insecticide belonging to a new acaricide pesticide family, the pyridazinones, which has been widely used on crops to control of mites and some other insects, such as white flies, aphids and thrips. Although pyridaben has been reported to be a substance of low toxicity to mammals, it still adversely affects their growth and reproduction, especially when it is used improperly [15–17]. Therefore, the rapid detection and determination of pyridaben is a practical necessity.

II. EXPERIMENT

Two main methods have been used to fabricate silver nanoparticles or nanostructures on silicon, namely electroless deposition (also called chemical deposition) and electrochemical deposition (also called electrodeposition). In the first method the silicon wafer, after being washed, is simply soaked in a suitable electrolyte solution for a certain period of time (usually from a few minutes to a few dozen minutes). The electrolyte solution is an aqueous solution containing $AgNO_3$ and HF in an appropriate proportion. In addition, this solution may also contain other components. A schematic diagram of the chemical deposition of silver nanoparticles or nanostructures on silicon is illustrated in Fig. 1a.

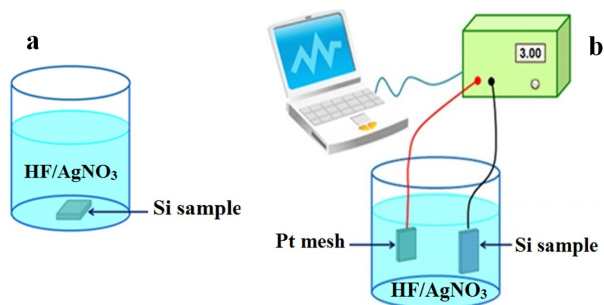


Fig. 1. Schematic illustration of the fabrication of silver nanoparticles or nanostructures on silicon either by chemical deposition (a) or by electrochemical deposition (b).

In the electrodeposition method, the aluminum-coated (on the backside) silicon wafer is connected to the cathode of a DC power source, while the anode of this power source is connected to a platinum grid, then the both silicon and platinum grid are immersed in an appropriate electrolyte solution for a certain period of time. The silicon used can be either *p* or *n* type and has a resistivity in the range of 0.1 to 100 Ωcm . In this method the electrolyte solution has almost

the same composition as that of a chemical deposition. The block diagram of electrodeposition is illustrated in Fig. 1b.

The fabrication of arrays of silver nanoparticles, nanodendrites or nanoflowers on silicon surface has been described in detail in our works [11, 15, 18, 19]. In brief, to produce an array of silver nanoparticles (AgNPs) on silicon, both chemical and electrochemical deposition can be used. More specifically, to chemically deposit AgNPs on Si surface, Si wafer was immersed in an aqueous solution containing 0.14 M HF and 5 mM AgNO₃ for 15 minutes at room temperature [18]. To electrochemically deposit AgNPs on Si surface, an electrochemical system has been established in which Si wafer acts as the cathode, while platinum grid serves as the anode. These two electrodes were placed parallel to each other and immersed in an ethanolic solution containing 0.1 mM AgNO₃ and 0.14 M HF. Silver electrodeposition on Si was carried out for 4 minutes at a constant temperature of 17°C under constant current mode, with a current density of 0.3 mA/cm² [11]. Note that before silver deposition, Si sample must be washed by soaking in ethanol (5 min), acetone (5 min), HNO₃/H₂O (1/1) (10 min), 5% HF (5 min) and deionized water (several times).

To fabricate arrays of silver nanodendrites (AgNDs) on silicon, the electrochemical deposition method was used. The electrochemical system with a silicon cathode and a platinum grid anode has been dipped in an aqueous solution containing 20 mM of AgNO₃ and 4.8 M of HF. The electrodeposition process was carried out under constant current mode with a deposition current density of 3 mA/cm² for 15 minutes at room temperature [15].

Silver nanoflowers (AgNFs) have been fabricated on the surface of Si wafers by the chemical deposition at room temperature. The Si sample was immersed in an aqueous solution containing 4.8 M HF, 1 mM AgNO₃, 10 mM ascorbic acid (AsA) and 5 mM polyvinyl pyrrolidone (PVP) for 10 min. After silver deposition, the samples were all washed with deionized water, then left to dry naturally in the air [19].

The Raman spectra of the samples were recorded either with a Raman spectrometer LabRAM HR 800 (HORIBA Jobin-Yvon, France) using a 632.8-nm laser as an excitation source or by a portable i-RamanPro spectrometer (model BWS475-785H produced by B&W Tek Inc., USA) with 785 nm excitation laser. The structure and morphology of representative silver nanoparticles or nanostructures samples were examined with a S-4800 field emission scanning electron microscope (SEM; Hitachi, Japan).

III. RESULTS AND DISCUSSION

Figure 2 presents SEM images with different magnifications of arrays of AgNPs that were chemically deposited (Fig. 2a and 2b) and electrochemically deposited (Fig. 2c and 2d) onto the silicon surface. It can be seen that, for the chemically deposited sample, the resulting AgNPs have a fairly uniform size of 50-80 nm, with an almost circular or oblong shape and they are fairly evenly distributed by a few tens of nanometers or more apart. Note that these AgNPs do not have to be on the same layer but can be superimposed. It should be emphasized that in the case when chemical deposition is replaced by electrochemical one combined with aqueous solution is replaced with ethanolic one then we can obtain a monolayer of AgNPs that are quite uniform in size and shape. Such an array of AgNPs is illustrated in Fig. 2c and 2d. As seen in these images, the electrochemically deposited AgNPs are much smaller (with sizes only of 20-40 nm) and they are arranged in a monolayer with the distance between neighboring particles being very small,

only a few nanometers. The density of these AgNPs is very dense and they evenly cover the entire Si surface.

As shown earlier, the deposition of AgNPs on the Si (AgNPs/Si) surface is a redox process in which Si is oxidized to a compound that dissolves into solution and silver ions are reduced to elemental silver that attaches to the Si surface in the form of nanoparticles. We believe that the reason for AgNPs to become smaller and more ordered in arrangement when using silver electrodeposition in an ethanolic electrolyte instead of water electrolyte is primarily because ethanol itself is also a mild reducing agent. Ethanol had the effect of reducing the rate of silver deposition on silicon and the deposition process became more controllable. In addition, the external current played the role of another factor that controlled the deposition of silver nanoparticles.

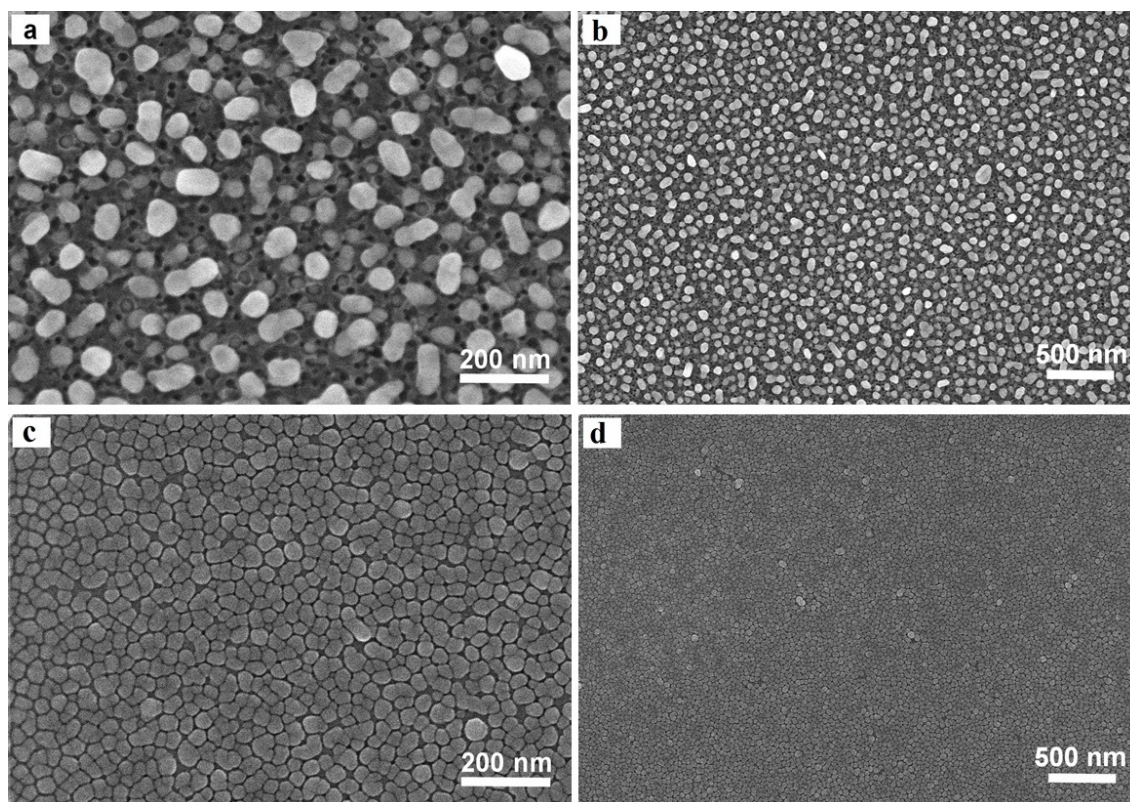


Fig. 2. SEM images of AgNPs/Si chemically deposited in an aqueous electrolyte (a, b) and electrodeposited in an ethanolic electrolyte (c, d).

In order to fabricate AgNDs on Si (AgNDs/Si), the most important thing is to change the ratio of HF/AgNO₃ accordingly. Both chemical and electrochemical deposition can yield AgNDs/Si, however electrochemical deposition will give AgNDs with better branching [18]. Fig. 3a and 3b show SEM images of AgNDs synthesized by electrodeposition with a current density of 3 mA/cm² for 15 minutes at room temperature, using an aqueous electrolyte containing 4.8 M HF and 20 mM AgNO₃. As we can see, after the deposition process, fern-like Ag dendrites with a size of about 100 μ m were formed on the Si surface. The structure of all AgNDs consists of a main

stem of about $100\ \mu\text{m}$ in size and sub-branches growing along both sides of this main stem. These sub-branches, in turn, can become the main stem with other sub-branches sprouting on either side of it. This branching process can continue to recur and thus a multi-level branching structure is formed (Fig. 3a). In addition, from the inset in Fig. 3a, the diameter of the smallest sub-branches is about 70-90 nm and the distance between two neighboring sub-branches is about 10-20 nm. The density of small sub-branches on a large sub-branch is quite dense. The SEM image with lower magnification shows that the AgNDs are randomly arranged in different overlapping layers and cover the entire Si surface (Fig. 3b).

In the literature, the mechanism of dendrite growth is often explained by two models of diffusion-limited aggregation (DLA) and oriented attachment (OA) [15, 20–22]. In short, AgNPs are firstly formed on the Si surface (according to the previously presented mechanism). Subsequently, the later-formed AgNPs diffuse towards the previously formed AgNPs and attach to them orientedly to form first a rod or wire structure, and then the dendritic structure.

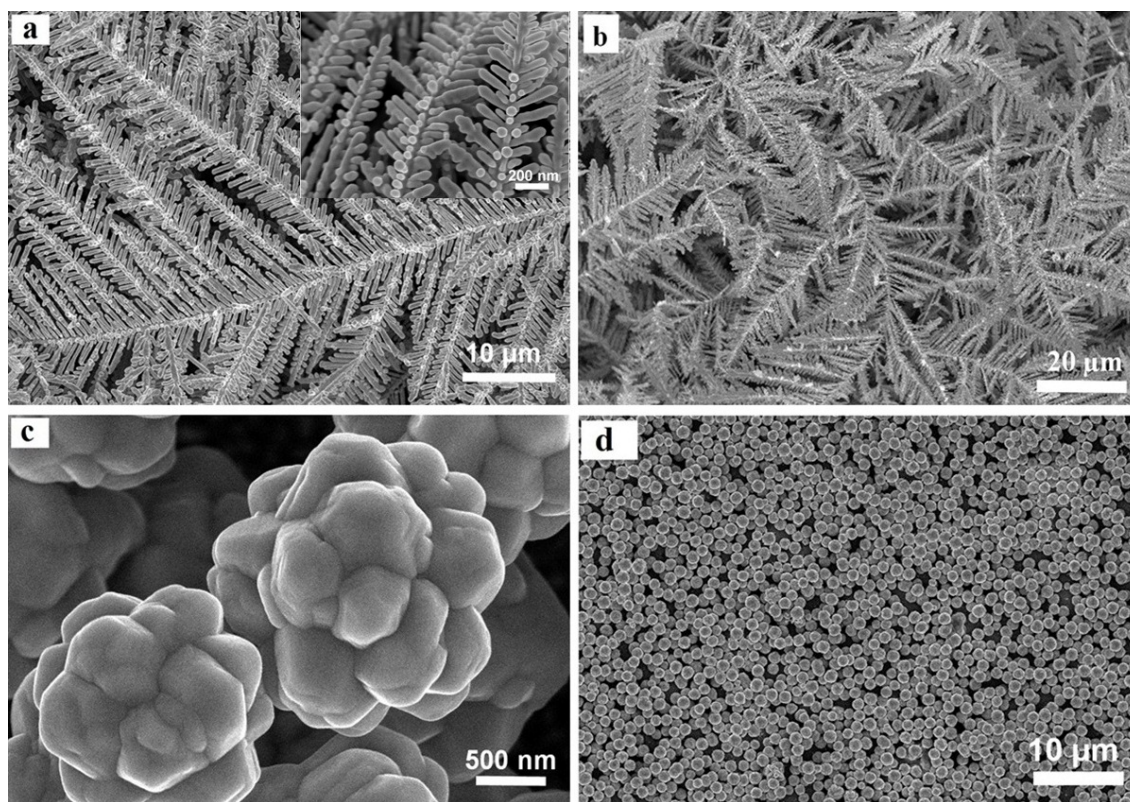
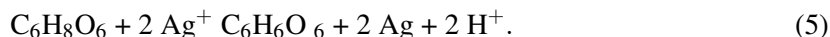


Fig. 3. SEM images of AgNDs@Si made with electrodeposition (a, b) and AgNFs@Si prepared by chemical deposition (c, d).

To fabricate silver nanoflowers on silicon (AgNFs/Si), chemicals such as those used in the synthesis of AgNPs and AgNDs are insufficient and others have been added. First of all, in addition to Si we added another reducing agent, namely, ascorbic acid (AsA). Note that AsA is used as the reducing agent in many AgNFs synthesis studies [23–25]. Furthermore, nano-flower structures

usually appear only when in the electrolyte there is an additional morphological directing agent like polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB) and the like. In this report, AgNFs prepared on Si by the chemical deposition in an aqueous solution containing 4.8 M HF, 1 mM AgNO₃, 10 mM AsA and 5 mM PVP at room temperature for 10 minutes [19] are shown in Fig. 3c and 3d. As it can be seen, the flower-like silver nanostructures with the size of 1.5 μm were formed on the Si surface after deposition. These AgNFs are highly rugged with many petals (Fig. 3c). They have good uniformity and cover the entire Si surface with a thick density (Fig. 3d).

The formation mechanism of AgNFs on Si surface in solution containing AgNO₃, HF, AsA and PVP can be explained as follows. In the reaction solution, silver ions are reduced simultaneously by Si (according to the mechanism described above) and AsA to form silver atoms. The reduction of Ag⁺ ions by AsA occurs according to the following equation [19, 23–25]:



As the reaction continues, more silver atoms are produced, which stick together to form larger nuclei. Next, PVP in the reaction solution will act as a capping agent that preferentially adsorbs on certain crystal surfaces of silver nuclei. As a result, the growth rate of these crystal surfaces is reduced compared to that of non-PVP absorbing crystal surfaces, which leads to an anisotropic growth of the crystal nuclei and the formation of flower-like structures [26].

Engineered structures have been used as SERS substrates for trace detection of a wide range of substances. The first target of detection is organic dyes, because the SERS technique is extremely sensitive to them. For example with AgNFs/Si SERS substrate we have detected crystal violet down to a concentration of 0.01 ppm [27], while with AgNPs/Si substrate, sudan I with concentrations as low as 1 ppb has been detected [18]. The next detection target is pesticides and other toxic substances. Specifically, with the SERS substrate made of AgNDs electrodeposited on silicon, we were able to detect the paraquat herbicide and the pyridaben and thiram pesticides to concentrations as low as 0.01 ppm, 0.1 ppm and 1.2 ppb, respectively [15, 20, 28]. Another example is that chemical deposited AgNFs/Si substrates have been used to detect trace of the toxic cyanide down to a concentration of 5 ppb [19].

Table 1. Band assignments of pyridaben [15].

Band (cm ⁻¹)	Assignment	Band (cm ⁻¹)	Assignment
635	δ(ring)	1106	ν(C-Cl); δ(C-H)
670	ν(C-Cl)	1138	ν(C-N); δ(C-H)
709	ν(C-S); (C-C-C), (C-C)	1200	δ _{tw} (CH ₂); ω(CH ₂)
710	ν(C-S); ν(C-C-C), δ(C-C)	1218	ν(C-N)
756	γ(C-H), ρ(CH ₂), δ(C-N)	1245	ν(ring); δ(C-H)
780	γ(C-H), ρ(CH ₂), δ(C-N)	1265	ν(ring); δ(C-H)
811	ν(C-Cl)	1280	ν(ring); δ(C-H)
846	δ(C-H)	1482	ν(C-N)
925	ρ(CH ₃)	1615	ν(C=C)
944	δ(C-H)	1648	ν(C=O)

ν stretching; ρ in-plane bending; out-of-plane bending; ρ rocking; δ_{tw} twisting; ω wagging

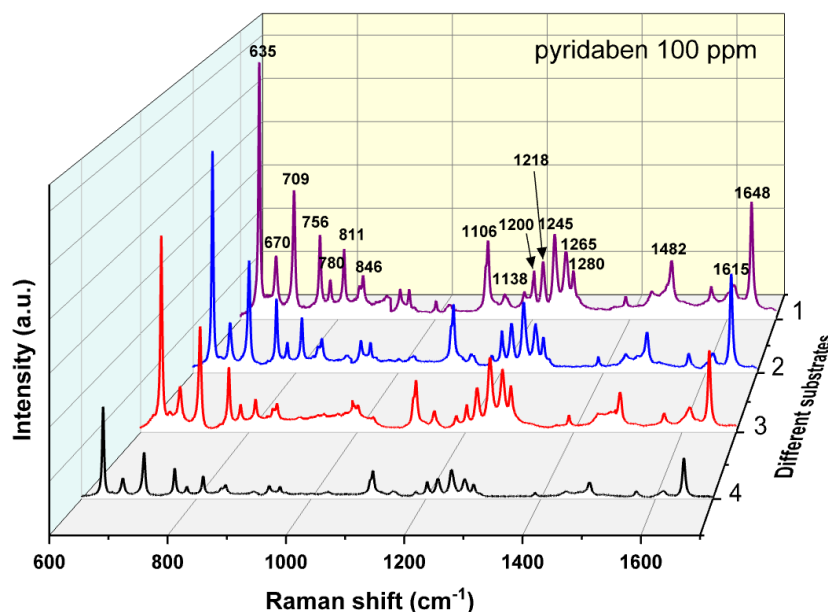


Fig. 4. SERS spectra of the commercial pesticide Koben 15 EC (containing 15% pyridaben) that was diluted to pyridaben concentrations of 100 ppm, which were obtained with AgNDs/Si (1), electrochemically deposited AgNPs/Si (2), AgNFs/Si (3) and chemically deposited AgNPs/Si substrates (4).

For illustrative purposes, below we will present the trace detection of the pesticide pyridaben by engineered SERS substrates. Fig. 4 shows SERS spectra of Koben 15EC, a commercial insecticide containing 15% pyridaben, diluted to pyridaben concentration of 100 ppm, obtained with AgNPs/Si, AgNDs/Si and AgNFs/Si substrates. First of all, it can be seen that the obtained SERS spectra all exhibit the same pyridaben-specific SERS peaks as shown in [15]. The fact that dilutions of the insecticide Koben 15EC exhibit only SERS characteristic peaks of pyridaben indicate that the additives in this commercial insecticide have no SERS activity or at least they do not cause bands in the region $600 - 1700 \text{ cm}^{-1}$. Table 1 lists the SERS characteristic peaks of pyridaben and their corresponding vibration modes. Specifically, the most intense peak at 635 cm^{-1} is assigned to the ring structure of the molecule while the second strongest peak at 709 cm^{-1} is due to the C-S stretching mode coupled with C-C-C stretching and C-C in-plane bending mode. The peaks at 670 , 811 , and 1106 cm^{-1} are attributed to the C-Cl stretching mode. The peaks at 1138 , 1218 , and 1482 cm^{-1} represent the C-N stretching mode. The peaks at 1245 , 1265 , and 1280 cm^{-1} are caused by the ring stretching and C-H in-plane bending mode. Another strong peak at 1648 cm^{-1} represents the C=O stretching mode and the band at 1615 cm^{-1} is due to the C=C stretching mode [16]. Next, it is evident that the AgNDs/Si substrate gives the highest SERS enhancement for the pyridaben molecules (curve 1). The SERS enhancement gradually decreased with the electrochemically deposited AgNPs/Si substrates, AgNFs/Si substrates and chemically deposited AgNPs/Si substrates, respectively. This result is understandable since AgNDs structure

is the one with the largest number of 'hot spots' (such as branch tips, nano gaps and intersections between neighboring branches as well as between overlapping branches).

Fig. 5 shows the SERS spectra of the insecticide Koben 15 EC diluted to different pyridaben concentrations in the range of 0.1 - 100 ppm, obtained with AgNDs/Si substrates. From Figure 5 we can see that when the pyridaben concentration in the analyte decreases, the intensity of the peaks of the SERS spectrum decreases steadily. When the concentration of pyridaben in the analyte is 0.1 ppm, the obtained SERS spectrum loses some characteristic peaks, but the peaks at 635, 709, 1265 and 1648 cm^{-1} are still observed quite clearly, allowing the confirmation of the presence of pyridaben. The fact that pyridaben can be detected in commercial pesticides at concentrations as low as 0.1 ppm opens up a new prospect for the use of SERS techniques to detect pyridaben residues in foods.

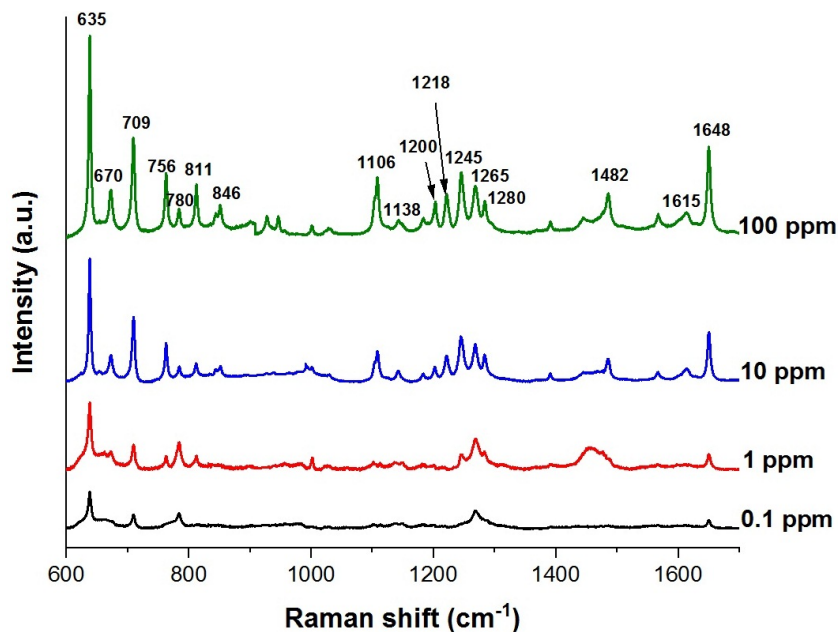


Fig. 5. SERS spectra of the commercial pesticide Koben 15 EC (containing 15% pyridaben) that was diluted to pyridaben concentrations of 100, 10, 1, and 0.1 ppm, which were obtained with AgNDs/Si substrates.

IV. CONCLUSION

In conclusion, for use as SERS substrate, a number of silver nanostructures including nanoparticles, nanodendrites and nanoflowers have been synthesized on silicon by two simple methods, chemical deposition and electrochemical deposition. Silver was chosen because it can give a SERS enhancement factor several times higher than gold. Silicon was chosen as the initial substrate for coating silver because it has a number of advantages, including its role in reducing silver ions. The aforementioned nanostructures were chosen because they are able to provide multiple hotspots with high hotness that are required to achieve great SERS enhancement. Examination of these structures as SERS substrates in trace detection of some substances, especially

pesticides, showed that they are good SERS substrates, normally they can detect pesticides down to 0.1 ppm concentration, while in some cases - down to ppb level.

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