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Fine-tunable plasma nano-machining for fabrication of 3D hollow nanostructures: SERS application

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Abstract

Novel processing sequences for the fabrication of artificial nanostructures are in high demand for various applications. In this paper, we report on a fine-tunable nano-machining technique for the fabrication of 3D hollow nanostructures. This technique originates from redeposition effects occurring during Ar dry etching of nano-patterns. Different geometries of honeycomb, double ring, nanotube, cone and crescent arrays have been successfully fabricated from various metals such as Au, Ag, Pt and Ti. The geometrical parameters of the 3D hollow nanostructures can be straightforwardly controlled by tuning the discharge plasma pressure and power. The structure and morphology of nanostructures are probed using atomic force microscopy (AFM), scanning electron microscopy (SEM), optical emission spectroscopy (OES) and energy dispersive x-ray spectroscopy (EDS). Finally, a Ag nanotube array was assayed for application in surface enhanced Raman spectroscopy (SERS), resulting in an enhancement factor (EF) of $5.5 \times 10^5$, as an experimental validity proof consistent with the presented simulation framework. Furthermore, it was found that the theoretical EF value for the honeycomb array is in the order of $10^7$, a hundred times greater than that found in nanotube array.

Keywords: Ar dry etching, electron beam lithography, nano-machining, 3D hollow nanostructures, surface enhanced Raman spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanometric machining (NM) [1]—ultrafine-tuning controllable nanoscale architecturing, alternatively classified under ‘top-down’ nanofabrication processes—allows manufacturing of nanoscale patterns and devices with fine accuracy and high reproducibility. One imperative advantage of NM is its applicability to the manufacture of a wide range of 3-dimensional (3D) complex architectures [2]. There are various NM techniques, based on atomic force microscope (AFM) [3], laser ablation and sculpturing [4–6], ion and proton beam writing and milling [7–10] and chemical or physical template assisted self-assembly of block copolymer (BCP) thin films [11].

Among many different 3D nanoscale artificial structures, hollow nanostructures have drawn an upsurge of attention in various fields such as nanoscale solar cells [12–14], materials [15], energy storage [16–18], electrolyt catalyst [19–21], biological sensors [22], photonic crystals [23] and metamaterials [15, 24, 25]. Hollow nanostructures can be manufactured [26–28] via tubular one-dimensional nanocrystals by rolling up layers [29], axial growth [30], coating pores in templates [31] or by eliminating the core of a core–shell nanowire [32]. However, these techniques are limited in the material...
categories, e.g. polymers or metals, and to a small fabrication area, and are thus ineffectual for 3D NM with tunable geometry. Therefore, a more reliable 3D manufacturing technique with fewer limits will be of prime interest to the scientific community, especially if it does not require new machinery. For example, a technique named as ‘secondary sputtering lithography’, enabling fabrication of 3D nanostructures via ion bombardment, was introduced recently [24–26]. In those reports, nanostructures are constructed by sputtering of material particles onto the sidewalls of pre-patterns.

Electron beam lithography (EBL) and colloid lithography [33–36] patterning with plasma etching are a well-established and accessible combination of NM techniques to fabricate 3D nano-elements. An extraordinary deposition—termed sidewall redeposition—occurs during plasma etching, resulting in standing materials deposited at the edges of final structures, able to be seen after resist removal [37]. This effect has so far been referred to as an annoying drawback. Here, we instead address this effect as a useful technique for the manufacture of nanostructures, fine-tunable by changing the plasma pressure and power. Such nanostructures offer a powerful way of surface enhanced fluorescence [38–40], and surface enhanced Raman [41, 42] effects.

In this paper, we explain how conventional EBL together with plasma etching techniques based on the redeposition effect can be employed for straightforward manufacturing of uniform 3D hollow nanostructures, for a variety of materials and geometries. We address plasma power and pressure as fine-tunable NM parameters, and discuss their mechanism in detail. Finally, the capability of our fabricated hollow nanostructure array for surface enhanced Raman spectroscopy (SERS) is presented, and compared with simulation for clarification.

2. Fabrication procedures

We carry out the fabrication of hollow nanostructures with two main steps: (i) the EBL of a resist deposited on top of an arbitrary substrate or thin film; and (ii) the Ar plasma etching. Figure 1 (all panels) schematically illustrates the steps in the fabrication of gold hollow nanostructures. First, a Au layer is sputtered on top of a glass slide. Then poly methyl methacrylate (PMMA), a positive electron resist, is deposited on top of the gold by the spin coating technique. Figure 1(A) shows this structure after holes are patterned by EBL on PMMA. Next, Ar plasma etching is employed to transfer the patterns onto the Au (figure 1(B)). Towards the end of this etching step Ar plasma etches the Au and PMMA layers simultaneously, and Au particles are redeposited on PMMA.

Figure 1. Schematic illustration of the NM fabrication process using plasma etching of Au-film and PMMA mask. This process results in redeposition of Au on the sidewalls of the etch mask. (A) step 1: generating desired pattern using e-beam lithography (EBL) on PMMA, (B-1) Ar plasma etching for transferring the patterns on Au and (B-2) redeposition of Au particles on PMMA side walls; (C) step 2: redeposition of particle on the side walls (C) step 3: hollow structures achieved after removing the resist.
sidewalls (figure 1(C)). Finally, well defined geometries of hollow nanostructures can be achieved after complete removal of the resist, (figure 1(D)). As compared to wet etching, such dry etching allows fine control of geometry (size, distance, material, thickness, etc) of the defined pattern. We will further elaborate on this issue later in this paper.

3. Results

3.1. Validity of the method

In order to evaluate the viability of this method, we have studied fabrication of a variety of hollow nanostructured materials including Gold (Au), Silver (Ag), Platinum (Pt) and Titanium (Ti). Interestingly, this method successfully showed well controlled patterns for Au, Ag and Pt (figures 2(A)–(C)). However, sidewall redeposition was not observed for the case of Ti. This can be attributed to the large Ti–Ti intermolecular bonds [43], i.e. the hardness, which is generally characterized by intermolecular bond strength. Notably, Ti has a higher hardness in comparison with the other noble metals (Au, Ag, …) [43]. In addition, some limitations are observed associated with aspect ratio of the hollow structures fabricated by NM technique. This can be explained by the difficulty of penetration of ion species into high aspect ratio structures [44].

The rest of this work will focus on physical mechanisms which lead to structures made of Au. Figures 2(D) and (E) show energy dispersive spectroscopy (EDS) analysis of the final pattern. Since EDS covers a broad volume of sample, there is no signal change at the position of the nanotube wall by line scan (as seen in figure 2(E)). Furthermore, there may be uncertainty in the position of e-beam in the point scans. This analysis reveals the presence of 98% Au and 2% Oxygen (for point EDS refer to figure 2(D); for line EDS refer to figure 2(E)). Despite the limitations of this method for nanoscale monitoring, it can be concluded from both scans that the sidewall is made of Au only, and there is no evidence of residual e-beam resist or any other materials at the sample surface adjacent to the nanotube.

Figures 3(A)–(E) and 4 show our fabricated nanostructures, including nanotube array, honeycomb structure, cone array, double ring array, nanohole array and crescent array, all prepared by the above NM technique. Actually, when holes in the prime pattern (obtained via EBL) are made to be close to each other the honeycomb structure can be made after Ar plasma etching, and as the holes become tangentially connected, the final product will be a cone array. Crescent arrays can be achieved by anisotropic etching of the substrate under a specific angle inside the etching chamber (schematic representation is shown in figure 4(A)). Under such circumstances, the redeposition rate increases at one side and decreases on the other side of the structure. Figure 4(B) shows the structure that is obtained when the substrate makes an angle of 22° with the electrode plate (which is in the plane), while figure 4(C) shows the same situation when the angle is increased to 30°.

The plasma parameters affect the dimension and geometry of the nanostructures, and the redeposition process can be hardly interpreted in terms of each parameter, individually. Changing any parameter can dynamically affect the whole plasma process. However, as our study is the first attempt to initiate and reveal this mechanism, the effect of varying the levels of one plasma parameter at a fixed level of other parameters is investigated here. In figure 5(A) (5 panels), scanning electron microscopy (SEM) images of patterns are shown for plasma etching effect with working pressure varied from 7 mTorr to 19 mTorr in the presence of Ar flow rate of 27 Sccm and plasma power of 70 W. The minimum working pressure for flow of 27 sccm is 7 mTorr, and increase in the pressure up to 19 mTorr is carried out to ensure that the redeposition effect has not occurred. The sidewall length determined from SEM and atomic force microscopy (AFM) are shown in figures 5(B) and (C), respectively—all taken after 2 min of plasma etching. Both SEM and AFM results (figures 5(B) and (C)) indicate that the sidewall length increases with increasing pressure up to 13 mTorr and decreases thereafter. Moreover, the etch rates for various Ar pressures are determined by measuring the etch depth of features using AFM results, shown in figure 5(D). It is found that the etch rate decreases between 7 mTorr and 13 mTorr, minimizes around 13 mTorr and then slightly increases. Our results indicate that decrease of etch rate corresponds to increase in the sidewall length. It can be concluded that the formation of fences in the plasma etching process is a consequence of the relatively low etching rate resulting from low ion bombardment. A further discussion on this issue is given in the next section.

Next, we explore the effect of the plasma power on the sidewall etch rate. Experiments conducted with plasma power of 40, 70, 100, 130 and 160 W, while the pressure was kept constant at 11 mTorr and processing time was held at 2 min. The same reason was applied for the selection of power range, as below 40 W there was weak plasma and all structures disappear above 100 W. SEM pattern of different plasma etching effect with working pressure varied shown for plasma etching effect with working pressure varied (figures 6(A), 6(B), 6(C), 6(D), and 6(E)), respectively. The same reason was applied for the selection of power range, as below 40 W there was weak plasma and all structures disappear above 100 W. SEM pattern of different plasma etching effect with working pressure varied shown for plasma etching effect with working pressure varied (figures 6(A), 6(B), 6(C), 6(D), and 6(E)), respectively. It is found that the sidewall length decreases with increasing plasma power. Figure 6(D) shows the Au etch rate increases with power, and the redeposition process on the sidewall of the photoresist decreases. The redeposition rate on the sidewall does not significantly occur for plasma powers above 100 W. This is evident from figures 6(C) and (D).

3.2. Fabrication analysis and discussion

In the following, we explain the details of the proposed NM process.

3.2.1. The effect of plasma pressure on the NM process. The etch rate was found to decrease significantly between 7 mTorr and 13 mTorr, minimized around 13 mTorr and then slightly increased up to 19 mTorr. Results of this investigation show that the redeposition rate is inversely proportional to the etch rate. The density of Ar ions was probed via optical emission
spectroscopy (OES) as a function of pressure (at a constant plasma power of 70 W). The emission intensity (of selected maximum 752 nm line) versus Ar plasma pressure, shown in figure 7(A), increases with pressure up to 13 mTorr, and then decreases a little thereafter.

The plasma processes could be divided into two different operating regimes [45] (shown in figure 7(C)). In one regime, the mean free path (MFP) for neutral ions is greater than the sheath thickness. Consequently, these ions are accelerated with negligible collisions toward the sheath. Under this condition, ions arrive with a nearly vertical velocity and produce vertical trenches (figure 7(C)-left). In the second regime, when the neutral/ions’ MFP is shorter than the sheath thickness the ions approach the surface with significant parallel velocity components (figure 7(C)-right). The parallel component allows ions to impinge on the sidewalls and produce a directional etch. The MFP, λ, for an atom or molecule having a cross section σ and density n is given by [46]

\[ \lambda = \frac{1}{n \sigma}. \]  

(1)

According to the ideal gas law, at 300 K, λ can be found by [47]:

\[ \lambda^{-1} = 3.22 \times 10^{22} p \text{(Torr)} \frac{1}{m}. \]  

(2)

where p is the pressure. The ion MFP has an inverse dependence on the pressure.

Figure 2. SEM images of the 3D hollow nanostructures of (A) Au, (B) Ag and (C) Pt hollow nanotube arrays at incidence angle of 70°. (D) point EDS and (E) line EDS measurements indicate presence of 98% Au and 2% oxygen.
Figure 3. SEM images of 3D Au hollow nanostructures for (A) nanotube array, (B) honeycomb nanostructures, (C) cone array, (D) double ring array and (E) nanohole array.
In the NM process, the ion energy distribution (IED) and ion angular distribution (IAD) determine the etch profile and etch rate [48]. The redeposition effect originates as a result of non-vertical etching. Thus, any changes in the IAD affect the redeposition effect. Elastic and charge exchange collisions in plasma affect both the IED and IAD in the sheath. A higher collision rate is associated with broadening of the IAD and reduction of the etch rate. Considering that the number of collisions is inversely related to the ion MFP, we conclude that a vertical etch is achieved at lower pressures and for ions with longer MFP.

To calculate the sheath thickness (details are available in the Method), the discharge current and radio frequency (RF) voltage are measured using voltage (Tektronix P6015 (1000:1V)) and current (Tektronix TCP202) probes over a gas pressure between 7 mTorr and 19 mTorr and plasma power between 70 W and 160 W. Schematic diagram of electrical measurements is shown in figure 8. MFPs and sheath thicknesses for various pressures are calculated and shown in table 1 and figure 8(B). According to these results, we find that whilst the ion MFP is larger than the sheath thickness (for plasma pressure from 7 to 13 mTorr), IED decreases while IAD increases with increasing pressure. The reason is that the MFP gets closer to the sheath thickness with increasing pressure. Therefore, the etch rate decreases and redeposition rate increases. Conversely, for pressures higher than 13 mTorr, the MFP becomes smaller than the sheath thickness (table 1) since more collisions occur. Therefore, density of ions in the sheath and consequently lateral etching is increased. Under this condition elastic scattering dominates over charge exchange collisions, resulting in a small increase in etch rate. This could yield small sidewalls due to enhancement of milling effect. Generally speaking, working at higher pressures—where the MFP is close to or larger than the sheath thickness—leads to the greatest NM productivity.

3.2.2. The effect of plasma power on NM process. Upon increasing plasma power, the Au etch rate increases as the redeposition rate decreases. This is shown in figure 7(B) where we observe that the maximum emission intensity (of the selected 752 nm line) increases when the plasma power increases and accordingly the etch rate increases. Both ion density and ion bombardment energy are controlled by RF power [49]. The ion current density in the sheath is given by [50]

\[ j_i = en_s u_B \]  

where \( n_s \) is the ion density at the presheath-sheath boundary and \( u_B = (KT/M)^{1/2} \) is the Bohm velocity.

Therefore, increase in plasma power leads to increase in the ion current density and the ion energy. According to equation (1), at constant temperature, the MFP only depends
on the pressure. Moreover, it has been previously found that the sheath thickness is independent of the total RF power delivered to the plasma [51] which is in agreement with our calculated sheath thicknesses for various powers (shown in table 2 and figure 8(C)). So by increasing the power, thickness is kept constant and smaller than the MFP. It is known that increase in the plasma power leads to increase in the plasma density (figure 7(B)) as well as increase in ion current density in the sheath (equation (3)) [49, 50]. Furthermore, the electric field increases in the sheath and consequently maximum energy of the IEDs increase as the plasma power increases [52, 53]. Thus, more ions get more energy when passing through the sheath resulting in increasing of the etch rate [54] (as we observe this effect in our
presented, figure 6(D)). A large angle is not physically possible in higher electric fields, since the direction of motion is dominated by the electric field direction [55]. So, angular distribution of ions becomes slightly narrower with increasing plasma power. As a result lower power is accompanied by lower ion mean energy and slightly higher IAD, which provides a higher redeposition effect (this is in agreement with our results). So, decreasing the power to the 40 W may be leads to a small shift of process window to the higher pressure value.

As explained above, any change in the IAD and IED caused by changes in the plasma conditions affects the redeposition effect. Since we know the effect of plasma power and pressure on the IAD and IED, we can guess the effect of each plasma condition (power and pressure) on the redeposition effect and consequently fabrication process.
3.3. Evaluation of the SERS applicability

Ag nanotube array is examined to investigate the SERS activity of our fabricated device. Toward this purpose, 15 μl droplet of the crystal violet (CV) with concentration of 1 μm is dropped on the substrate and permitted to dry. SERS measurement is performed using Raman microscope device and the acquired result is shown in figure 9.

For calculation of the enhancement factor (EF), first the fluorescence baseline is removed using an iterative multipolynomial fitting algorithm [56]. The experimental EF value is calculated by the following equation [57]

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{ref}}} \cdot \frac{N_{\text{surf}}}{N_{\text{bulk}}}
\]  

where \( I_{\text{SERS}} \) and \( I_{\text{ref}} \) are the surface enhanced Raman intensity (from SERS spectrum) and the Raman intensity (from reference spectrum) of the characteristic peak, respectively, \( N_{\text{surf}} \) and \( N_{\text{bulk}} \) are the number of molecules within the excitation.
region of the analyte on the SERS substrate and the reference substrate, respectively. The number of molecules \( N \) is given by

\[
N = \frac{N_A CV_{\text{laser}}}{A_{\text{spot}}}
\]  

(5)

where \( A_{\text{laser}} \) is the area of the excitation laser spot, \( A_{\text{spot}} \) is the total area of the probe molecules on the each substrate, \( V \) is the volume of the CV drop, \( N_A \) is Avogadro’s number and \( C \) is the molar concentration of the CV analyte.

We precisely calculate the EF of the substrate by comparing the intensity of CV Raman peak at wavenumber

*Figure 8.* (A) Schematic diagram of electrical measurement. The calculated sheath thickness and mean free path for (B) various powers and (C) various pressures.

<table>
<thead>
<tr>
<th>Pressure (mTorr)</th>
<th>7</th>
<th>11</th>
<th>13</th>
<th>15</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_s ) (mm)</td>
<td>3.0</td>
<td>2.8</td>
<td>2.6</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>MFP (mm)</td>
<td>4.77</td>
<td>3.03</td>
<td>2.75</td>
<td>2.2</td>
<td>1.75</td>
</tr>
</tbody>
</table>

*Table 1.* The calculated sheath thickness and mean free path for various pressures.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>70</th>
<th>100</th>
<th>130</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_s ) (mm)</td>
<td>2.8</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>MFP (mm)</td>
<td>3.03</td>
<td>3.03</td>
<td>3.03</td>
<td>3.03</td>
</tr>
</tbody>
</table>

*Table 2.* The calculated sheath thickness and mean free path for various powers.

*Figure 9.* SERS spectrum of CV molecules for the concentration of 1 \( \mu \)m on the Ag nanotube array substrate with power of 8 mW and integration time of 15 s. Inset shows crystal violet molecule.
590 cm\(^{-1}\). The CV solution, with concentration of 78 mm, is deposited on a glass substrate as a reference. Our calculation shows the EF value of 5.5 \(\times 10^3\) for this nanotube substrate. It should be noted that optimization of the geometrical parameters of the Ag nanotube array leads to higher EF.

### 4. Discussions

Our manufacturing route enables us to control the nanostructures’ shape (nanotube, nanocrescent and nanocone arrays) and geometrical parameters (height, radius and thickness). Such fine-tuning is useful in the investigation of optical response of the final nanostructures. To accomplish this, a finite difference time domain (FDTD) method is used to estimate the EF of nanotube arrays with various shape and geometrical parameters. Near field strength at hot spots (maximum local electric field) [58] is a significant factor determining the amount of EF signal. In other words, maximum near electric fields determine the amount of maximum electromagnetic EF. For this reason the electromagnetic fields are calculated at the excitation wavelength (532 nm). The EF approximate factor is commonly used for calculation of EF [59, 60]. So for calculation of the electromagnetic EF, maximum local electric field \(E_{\text{loc}(\omega_{\text{ex}})}\) at the excitation wavelength is considered (532 nm—for modeling details see Method section). In figure 10(A), we demonstrate the height dependence of the EF for various outer radius (O.R) and inner radius (I.R) values (periodicity is fixed to be 500 nm). It is known that different combinations of geometrical parameters change the type and wavelength position of resonance modes, and as a result different electromagnetic field enhancements can be obtained. As seen in figure 10(A), the EF of the nanotube array with geometrical parameters of \(h = 175\) nm and \(O.R = 225\) nm (similar to dimensions of the fabricated nanotube array) is in the order of \(10^3\), which is in agreement with the EF obtained experimentally. As can be concluded, there is good consistency between simulation and experimental results for the nanotube array, to achieve EF of \(10^3\). Additionally, we show that our method is able to control the dimensions of the nanostructures. So, to reduce the risk of manufacturing, we now report on simulation results only, to predict the structure with highest EF which will be manufactured in our future work. From the acquired results (figure 10(A)), it can be observed that the best nanostructure to achieve the maximum EF is the honeycomb array. Figure 10(B) shows the behavior of the reflection spectra for a Ag honeycomb array with \(O.R = 250\) nm and \(I.R = 200\) nm for different heights. It is seen that a wavelength red shift occurs when the height is increased. For a height of 200 nm, the resonance mode is overlapped with the excitation wavelength (532 nm—figure 10(B)), which leads to the maximum EF. The electric field and EF distributions for this honeycomb structure are shown in figure 10(C). It is observed that the field is concentrated in the sharp gap between nanotubes, due to the lightning effect [40, 41]. As explained above, the EF is proportional to the fourth power of the electric field amplitude enhancement, so the honeycomb structure has the EF up to \(10^7\) for dimensions considered in this simulation (as shown in figure 10), which is a hundred times greater than the nanotube array EF (which about \(10^5\)). Our simulation results indicate that the minimum near 500 nm in reflection spectrum originates from localized surface plasmon resonance (LSPR). According to previous reports, nanotip and nanoring structures provide significant field enhancement effects [42, 43]. Therefore, large EF enhancement can be obtained from our nanocrescent array (consists of both nanoring and nanotip on the sharp edge) and nanocone array [44, 45].

### 5. Conclusions

In summary, we have proposed a novel NM method for fabrication of 3D hollow nanostructures by the fine control of the redeposition rate, a phenomenon normally referred to as a major drawback in nanoscale manufacturing. This nanofabrication method can be readily extended to a wide range of materials and geometries. As compared with other methods, the proposed approach is easier to conduct if fabrication of hollow nanostructures is of interest. Furthermore, no specialized machinery is needed for this purpose. The plasma power and pressure are critical parameters in this 3D nanofabrication process effect; these were investigated and optimized for the SERS nanostructures studied in this paper. Finally, the SERS spectrum of a Ag nanotube array has been measured, and EF of \(5.5 \times 10^3\) obtained. Our simulation results indicate that the various EF can be obtained by tuning the geometrical parameters of our nanostructures, and that the honeycomb structure provides higher EF as compared with the nanotube array.

### 6. Methods

#### 6.1. Electron beam lithography technique

The samples were coated with 200 nm Au over 5 nm Ti adhesion layer on glass substrates. A 300 nm thin layer of PMMA was used as an EBL-resist. The EBL capability was achieved by incorporating a purpose built pattern exposure system employing a TESCAN VEGA SEM. EBL process was carried out under the following conditions: accelerating voltage of 15 kV, e-beam spot size of 21 nm and electron dose of 500 \(\mu\)c cm\(^{-2}\). After EBL, the samples were developed in a 1:1, methyl-isobutyl-ketone (MIBK) and Isopropyl Alcohol (IPA) mixture, for 1 min. Next, they were rinsed in IPA immediately after developing and dried by clean air.

#### 6.2. Argon etching

Experiments including resist masked Au etching were performed by using a physical ion etcher. The RF reactor operating at 13.56 MHz in a parallel plate capacitively coupled configuration was used to generate plasma from Argon. The flow rates for Ar were controlled electronically using mass
flow controllers. The working pressure varied from 7 to 19 mTorr by throttle valve positioned at the entrance of the pumping system, and RF power was adjusted between 40 and 160 W.

6.3. Plasma parameters measurement

The lower electrode was powered by RF while the discharge chamber was grounded. To exhibit the waveform of the discharge current and RF voltage two channel digital oscilloscope (Tektronix DPO3012 100 MHz 2.5 GS/s) is used. The voltage $V$ is measured by Tektronix P6015 (1000:1V) probe, while the discharge current $I$ is measured by Tektronix TCP202 probe.

6.4. Characterization

The morphology and size dimension of the nanostructures were investigated using field emission SEM (TSCAN MIRA II) operated at 15 kV. The images were taken by secondary electron emission detector at 8 mm working distance. The composition of the structures was analyzed by the SEM equipped with an energy dispersive x-ray analyzer (EDXASMX). The etch rates, heights and widths of nanostructures were examined by AFM Nova PX (NT-MDT) in non-contact mode.

For OES, the light emitted from the plasma was collected through vacuum chamber window by an optical fiber with 250 μm in diameter. The optical fiber was placed in front of

![Figure 10](image-url)
the window and connected to a detection device. The optical emission spectra were registered using an Ocean Optics spectrometer model HR2000+ equipped with an entrance slit of 15 μm, grating of 300 grooves mm⁻¹ and and charge-coupled device (CCD) detector. The measured spectra were obtained in the wavelength range of 200–1100 nm with the optical resolution of 1.5 nm. For data collection and storage, the software Spectrasuit was used.

6.5. SERS measurements

SERS spectrum is measured by Raman microscope spectrometer (Tekscan N1-541-Iran) using a CCD detector with the resolution of 1 cm⁻¹, excitation wavelength of 532 nm, power of 8 mW and integration time of 15 s.

6.6. Sheath thickness calculation

According to [61], the sheath thickness is calculated using the following equation (capacitor formula)

\[ C_s = \frac{\varepsilon_0 A}{d_s} \]

where, \( A \) is the electrode area, \( d_s \) is the sheath thickness and \( C_s \) is the sheath capacitance. The relationship between the sheath capacitance and capacitive reactance of the sheath (X) is given by

\[ X = -\frac{1}{\omega C_s} \]

\[ d_s = \omega \varepsilon_0 A |X| \]

\[ |X| = \frac{V_{RF}}{I} \]

where, \( V_{RF} \) is the RF voltage and \( I \) is the discharge current.

A schematic diagram of electrical measurement and an example of the waveform of RF discharge are shown in figure 8. Diameter of the electrode is 15 cm. Sheath thickness for various pressures and powers are calculated using the above equations and is shown in tables 1 and 2 and figure 9.

6.7. FDTD simulation

A 3D FDTD method is used to estimate the EF of our nanotube structure with various geometrical parameters. Periodic boundary condition in the x and y directions and perfect matching layer (PML) in the z direction are considered. A linearly polarized plane wave with a wide frequency range illuminates the unit cell along the –z direction. The polarization of incident field is aligned along the x axis. The dielectric function of Ag and silicon is taken from Palik handbook. For estimation of the theoretical EF, near electric field distribution are calculated at the excitation laser wavelength (532 nm), and the approximation \(|E_{loc}/E_0|^4\) is used.

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