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A novel preparation method for uniform large-area graphene films on Ni@Cu substrate

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Graphical Abstract

Highlights

• Graphene film is prepared by CVD method on the Ni/Cu substrate.
• Using sputtering and CVD annealing process to prepare the Ni/Cu substrate.
• The effect of cooling rate on the growth of graphene film was studied.
• Graphene film has the advantages of large-area, high quality and uniform growth.
• The number of layers of graphene film was regulated by the compositing of Ni atom.

Abstract:

Controlling the number of graphene layers is crucial in graphene synthesis for the development of graphene-based electronics. Numerous investigations have found that a reasonably designed binary alloy can effectively overcome the defects of pure metal
and activate the self-limited growth of a monolayer of graphene. Graphene films were prepared on the Ni@Cu substrate by a chemical vapor deposition method. Ni@Cu is a novel Cu based substrate whose surface is alloyed with Ni atoms. In this paper, the advantages of graphene film synthesis on this new substrate were demonstrated through experiments, including the influence of the fast cooling process on the growth of graphene film, the influence of the proportion of Ni on the growth thickness of graphene film, and the transfer process of graphene film from this substrate.

**Keywords:** Chemical vapor deposition; sputtering; multilayer structure; Raman; thin films

1. **Introduction**

Graphene is a two-dimensional monolayer of sp2-hybridized carbon atoms. Because of its remarkable chemical and physical properties [1], it has been widely investigated for the development of novel high-performance transistors, sensors, actuators and so on [2, 3]. For practical applications, a controllable, reproducible and large-area production of graphene is of vital importance. The features of a graphene film depend sensitively on the film thickness. For instance, monolayer, bilayer, and tri-layer graphene film have different properties [4, 5]. Therefore, controlling the number of graphene layers is crucial in graphene synthesis for the development of graphene-based electronics. The chemical vapor deposition (CVD) technique has become the most promising approach because it is inexpensive, transferable for the preparation of high-quality graphene film. However, it is difficult to control the number of graphene layers owing to some serious obstacles [6, 7].
The Cu is a suitable substrate for the preparation of large-area monolayer graphene film [8]. Due to its catalytic mechanism of self-limiting, Cu substrate as the catalyst is difficult to achieve controllable preparation of graphene films [9]. Also, a previous report reveals that under atmosphere pressure CVD, the graphene growth on a Cu surface is not self-limiting any more [10]. Some studies used a Cu as a catalyst to synthesize graphene film with different layers by changing experimental parameters [11, 12]. However, the growth of graphene films by the CVD method is affected by a variety of factors such as substrate temperature (T_s), pressure, deposition time, and the flow ratio of the hydrocarbon source. Recently, using a Cu or Ni substrate as catalysts have been demonstrated to effectively synthesis large-area monolayer and multilayer graphene structures. Numerous investigations have found that a reasonably designed binary alloy can effectively overcome the defects of pure metal and activate the self-limited growth of a monolayer of graphene [13-15]. Graphene films with different layers have been fabricated by changing the proportion of the metals in the binary alloy substrate such as in the Cu-Ni alloy [16]. These studies have shown that the researchers first deposited a layer of Ni on the Cu substrate, then alloyed the substrate by keeping it at 1000~1075 °C for enough time (1~6h) to allow the Ni atoms to fully and uniformly diffuse into the Cu substrate: the longer the alloying duration, the deeper the Ni atoms diffuse. Finally, the graphene films were synthesized on this alloy substrate.

Through systematic experimental, we found several relative deficiencies in this process: a) The researchers obtained a uniform alloy phase by extending the alloying time of the substrate. However, the surface of the polished Cu substrate at the semi-
melting temperature for a long time will cause certain damage to the smooth surface state, and the surface roughness will increase, which is not conducive to the uniform growth of the thin film. b) The Cu atoms in the Cu-Ni phase inhibited the over-saturated precipitation of carbon atoms during the cooling process. Therefore, a part of carbon atoms will be fixed in the alloy phase and crystallize with Cu atoms. These carbon atoms will form impurities to adsorb on the graphene film after the wet chemical transfer process. It also directly affects the electrical properties of graphene films. c) The Cu-Ni alloy substrate has an excellent corrosion resistance because of Cu atoms in the Cu-Ni phase can improve the passivation protection of the substrate [17]. Therefore, transferring a graphene film from the surface of Cu-Ni substrate is more complex than transferring a graphene film from the surface of the Cu substrate. d) To save the purchase of alloy substrate, this process is widely used, but it still consumes a lot of electrical energy, and the alloying process needs to be carried out in the mixed atmosphere of H₂ and Ar. From the perspective of energy saving and the economy, the cost is not small.

In this paper, the main content is divided into four key points: 1) The diffusion depth of Ni atoms is reduced by reducing the annealing time. 2) To make the Ni atoms more evenly distributed on the surface of the Cu substrate, we improved the process by rotating the substrate in the sputtering and by reducing and increasing the RF power and sputtering time to a certain extent, respectively. 3) To improve the crystalline quality of graphene and control the number of layers, a rapid cooling process was used after the CVD deposition stage to reduce the substrate temperature from 1050 °C to 600 °C.
at an extremely rapid rate. 4) The controllable preparation of graphene films was realized by using the improved process. We found that the cooling rate has a great influence on the crystallization of graphene film, which not only affects the crystallization of the graphene film but also has a great impact on the number of layers. Through such a design, we only need to change the sputtering time of Ni to obtain a series of Ni/Cu substrates and prepare graphene films with a different number of layers on these substrates. A uniform alloy surface phase without preparing the entire alloy body phase has been created. The substrate is neither a nickel-copper layered structure nor a fully alloyed substrate, so we named it Ni@Cu. This process reduced the corrosion difficulty of the substrate in the transfer process and can avoid the carbon atoms excessively dissolve into the substrate, hence to reduce the carbon atom impurities generated.

2. Experimental work

2.1 Preparation of graphene sample

Ni@Cu substrate was prepared by two steps. Firstly, Ni/Cu was prepared by RF-magnetron sputtering method using a Ni target and a polished mono-crystalline Cu (111) substrate (99.9% purity, with dimensions of 10*10*0.5 mm³). During the sputtering process, the working pressure, RF power, T_s, and the flow of Ar were maintained at 1.5-2.0 Pa, 150 W, 400 °C, and 20 SCCM, respectively. Also, the substrate rotation speed was set to 1.5 rpm. Four Cu substrates were sputtered 25, 50, 75, 100 min, respectively. Secondly, the samples will be alloyed with the CVD method. The structure of the CVD system is shown in Fig.1c. Before heating up, argon (50 SCCM) was inlet
into the quartz-tube to remove air impurities after the pressure in the tube was reduced to -0.1 MPa by a mechanical pump. Then, the substrate is heated to 1050 °C with Ar inlet. H₂ (100 SCCM) was injected for 28 minutes to form surface alloying when the temperature is stable. The surface alloyed substrate was called Ni@Cu. Next, directly began the growth of graphene films. Ar (600 sccm) and the hydrocarbon mixture of C₂H₂/H₂ (10 sccm/100 sccm) was passed into the airway for 600 s during the deposition. In the cooling stage, a radiator fan was used to make the Tₛ falling fast, as shown in Fig.1a, the cooling rate of Tₛ was 42 °C/min in the 1050 °C-600 °C interval and was 25 °C/min in the 600 °C-20 °C interval.

2.2 Characterization

In this paper, X-ray diffraction (XRD, Shimadzu 6100) was used to characterize the Ni/Cu substrate, whereas Raman spectroscopy (Renishaw inVia, 514nm laser excitation) was used to characterize the quality and layers of graphene films. Scanning electron microscopy and energy dispersive spectrum system (SEM+EDS, Phenom ProX) were used to characterize the surface state of the substrate. The Raman line-scan of graphene films were characterized by Raman spectroscopy (LabRAM HR Evolution-Horiba Scientific, 532nm green laser).

3. Results and discussion

3.1 The effect of cooling rate on the growth of graphene films

Raman spectroscopy is a powerful non-destructive technique for identifying the number of layers, structure, doping, and disorder of graphene [18]. Graphene has three
Raman characteristic peaks in D band (1350 \textsuperscript{-1}), G band (1580 \textsuperscript{-1}) and 2D (2700 \textsuperscript{-1}) band \cite{19, 20}, respectively. The defect level of any graphene film was further evaluated by the intensity of the D band (I_D), the value of full width at half maximum of 2D band (FWHM \textsubscript{2D}) and the ratio of intensity of the G band (I_G) to that of the 2D band (I_{2D}) characterizing the thickness of the graphene film \cite{21}. In this study, the samples were cooled using three different cooling rates under the same deposition process parameters. As shown in Fig. 2, an interesting phenomenon has been found in the investigation of the relationship between the thickness of graphene film growth and the cooling rate.

The cooling rate was controlled by a slide heating unit (SHU) and a cooling fan, Fig. 1c shows the position of SHU and cooling fan. The SHU moves through a guide rail below it, and the cooling fan is fixed to the right of the SHU. The substrate is located in the middle of the SHU during heating and deposition. To speed up the cooling rate during the cooling process, the SHU will move left so that the substrate can be located above the cooling fan. As shown in Fig. 1b, the cooling rate of slow cooling (do not move and turn on the SHU and fan), moderate cooling (mobile the SHU, do not turn on the fan) and fast cooling (mobile the SHU and turn on the fan) in two temperature intervals were calculated in Fig. 2b. As shown in Fig. 2, the G band and 2D band for the slow cooling process (blue curve) were not obvious at all. As shown in Fig. 1b, it took more than 3 hours for the T_S to drop from 1050 °C to 600 °C during the slow cooling process. We inferred that the excessive cooling time will make the carbon atoms forming an amorphous graphite layer in a continuous high-temperature environment. By analyzing the literature, we found that the conclusion of one study could well
support our inference. Maxwell Z et al. have studied the metal-catalyzed crystallization of amorphous carbon to graphene: excessive alloying time will cause amorphous carbon to fail to form graphene, and the Raman cannot detect carbon atoms on the substrate surface [22]. The curve (b) in Fig. 2b shows graphene films, in the case of moderate cooling. The G band and 2D band of graphene are obvious for this case: the crystallization of graphene has been affected by the accumulation of carbon atoms. As shown in Fig. 1b, the cooling time from 1050 °C to 600 °C has been reduced to less than 1 h. The value of $\frac{I_{2D}}{I_G}$ and the FWHM$_{2D}$ band is 0.84 and 52 cm$^{-1}$. Meanwhile, the D band can hardly be observed from curve (b), which indicates that the graphene film has an excellent crystallization quality. For the fast cooling process (see curve (c)), where the cooling time from 1050 °C to 600 °C is shortened to 10 minutes, the value of $\frac{I_{2D}}{I_G}$ and FWHM$_{2D}$ is 3 and 32 cm$^{-1}$, respectively, which corresponds to monolayer graphene. This fast cooling process reduces the continuous accumulation of carbon atoms. The above three kinds of experiments were all carried out under the condition of constant external temperature and humidity, and the vacuum pump was always turned on before the end of the cooling process. This process was applied to the preparation of graphene films on Ni/Cu substrate. The fast cooling process can effectively reduce the excessive precipitation of carbon atoms at the grain boundary of the alloy.

3.2 Preparation of the Ni/Cu substrate

Fig. 3a-d show the different Ni/Cu substrates were prepared by a sputtering method with different sputtering time. It can show that with the increase of sputtering time, the morphology of nickel atoms gradually changes from island to thin film.
Subsequently, four substrates were alloyed by CVD and graphene films were prepared on Ni@Cu substrate. As shown in Fig. 4a-d, the Ni atoms were sputtered onto four Cu substrate surfaces for 25, 50, 75, and 100 minutes, respectively. The growth model of the thin film is an island growth model in the sputtering process [23]. The distribution of Ni atoms on the Cu substrate was chaotic. Fig. 4e-h show the surface morphology of the Ni@Cu substrates after the CVD alloying process without deposition of the carbon atoms. CVD alloying process reconstructed the Cu and Ni atoms into new surfaces. Fig. 4i shows the XRD spectra of different Ni@Cu substrates (after CVD alloying). It is clear from this figure that all the diffraction peaks shift to the right and close to the Ni with an increase of the sputtering time. As shown in Fig. 3j, it can be proved by randomly selecting peak (200) in Fig. 3i. We found from Fig. 4 that the Ni atoms will incorporate into the Cu substrate phase due to lattice thermal expansion when $T_s$ is 1050 °C.

The shifting of the XRD diffraction peaks can prove that the strength of the alloy increases with the sputtering time. Two studies used similar methods to make alloy phases: Y. Takesaki et al [24]. have used evaporation method to deposit Ni film with 100 nm thickness on Cu film with 400 nm thickness, then, the substrate was alloyed by CVD for 2 hours to make Ni atoms blend into the Cu film phase at 1075 °C; G. Lu et al [25]. have used electro-plating to cover the Ni film on the Cu foil as substrate, then, alloying the substrate for 2 hours to prepare Cu-Ni phase in H₂ atmosphere at 1050 °C. These studies also have shown that the longer the alloying time is, the more evenly the Ni atoms dissolve into the Cu substrate phase, and the short alloying time will result in
the inhomogeneous dispersion of Ni atoms in the Cu phase.

In this study, the alloying time was set less than 30 min to reduce the infiltration of Ni atoms and restrict the alloying of the Ni/Cu substrate. There are two ways to ensure the uniformity of substrate surface alloying: The RF power was limited to 150 W to reduce the sputtering efficiency and cluster the diameter of Ni atoms during deposition; Rotating the substrate allows to improve the uniformity of the distribution of Ni atoms on the surface of the Cu substrate. Next, EDS was used for quantitative analysis of the surface of Ni@Cu substrate. As shown in Fig. 5, the SEM-EDS system can directly obtain the EDS spectrum and the atomic percentage of images from Fig. 4e-h. It can be found that the Ni atomic percentage of different Ni/Cu substrates increased for a larger sputtering time. For a sputtering time of 100 minutes, the atomic ratio of Ni atoms on the surface reached 8.1% after the CVD alloying process. It can be seen from Fig. 3 that most of the surface of the Cu substrate has been covered by Ni atoms, while Fig. 5b shows that only 8.1% Ni exists on the surface of the Ni@Cu which was sputtered for 100 minutes, which indicates two points. This indicates that the substrate surface alloying is obvious.

3.3 Controlled preparation of graphene films on the Ni/Cu surface

It is well known, the catalytic mechanism of Cu substrates on the growth of graphene film is adsorption and self-limit [26]. The carbon atoms will diffuse on the substrate surface and be atomically adsorbed with Cu atoms to form a graphene film. The part covered by carbon atoms on the Cu surface will not absorb any other carbon atoms. Therefore, the thickness of graphene films grown on Cu substrates is
independent of the deposition time but related to the concentration of the carbon source [27]. The smaller the carbon clusters adsorbed during the deposition process, the thinner and more uniform the grown graphene films. Fig. 4a shows the Raman spectrum of graphene prepared on the Cu (111) substrate. The value of I_G/I_2D in Fig. 1a is 0.46 and the FWHM (2D) is 33 cm^{-1}, which perfectly corresponds to a monolayer of graphene. The fast cooling process was used in this preparation process. The hexagonal honeycomb structure of carbon atoms can be seen from the SAED in Fig. 4b. As the thermal expansion coefficient of Cu is larger than that of graphene, the lattice contraction of the surface of the Cu substrate will cause the graphene film to shrink and generate wrinkles after the cooling process.

Fig. 5 shows the Raman spectrum of graphene films, prepared on different Ni@Cu substrates. The values of I_D/I_G, I_G/I_2D, and FWHM_{2D} from the Raman curve (a)-(d) in Fig. 5 have been calculated in Table 1. The values of I_D/I_G in Table 1 are less than 0.1, which correspond to high-quality graphene films. By comparing the value of I_G/I_2D and FWHM_{2D}, it can be seen that the higher the content of Ni atoms on the surface of the Cu substrate, the thicker the grown graphene film. In general, Ni can effectively catalyze the carbon source at a low T_S (600 °C-) in CVD process due to the solution-precipitation catalytic mechanism [28]. When T_S > 600 °C, the carbon atoms will dissolve into the metal phase due to the expansion of the Ni lattice, and then the carbon atoms will precipitate out of the Ni metal surface with the shrinkage of the lattice during the cooling process to form the graphene film. The longer the deposition time, the more
carbon atoms dissolved into the Ni substrate phase. For the catalytic mechanism of Ni@Cu substrate in the CVD growth of graphene films, the growth of graphene is determined by the co-catalysis of Cu and Ni: carbon atoms can dissolve into the substrate phase due to the strong catalytic effect of Ni during the deposition stage; Due to the effect of atomic force adsorption, Cu atoms will have a fixed effect on carbon atoms dissolved into the substrate phase, thus inhibiting the excessive precipitation of carbon atoms and improving the uniformity of growth of graphene films.

According to the Raman curve in Fig. 7 and the data in Table 1, the value of FWHM\textsubscript{2D} and \textit{I}_G/\textit{I}_2D of curves (a) to (d) are increasing, which can preliminarily prove that the number of layers of graphene films is increasing. For example, the value of the \textit{I}_G/\textit{I}_2D and FWHM\textsubscript{2D} of the curve (a) are 0.69 and 38.79 cm\textsuperscript{-1} and in the curve (c) are 1.41 and 55.61 cm\textsuperscript{-1}, respectively. This indicates that curve (c) represents a few-layer graphene film. However, the number of graphene films grown on the surface of pure Cu (111) substrate under the same process is a single layer. The wet-chemical method was used to transfer graphene film of the curve (c) to SiO\textsubscript{2}/Si substrate surface, and then to find out whether the number of layers on the surface of the film was uniform. High-resolution Raman line-scanning technology can effectively characterize the uniformity of graphene films. As shown in Fig. 8, we randomly selected a straight line on the sample surface and captured along that line at 10 different locations a Raman spectrogram. The 10 values obtained for the \textit{I}_G/\textit{I}_2D ratio along that line are shown in Table 2. The data in this table show that compared with the pure Cu sample in Fig. 6, the layer number of the film on this sample is increased and the uniformity is ideal.
As shown in Fig. 9a(a), Cu-Ni substrate is obtained by CVD annealing with a long time for Ni/Cu substrate. CH₄ will be catalyzed by Cu and Ni on the substrate surface, and the carbon atoms will dissolve into the alloy phase from the surface of the Ni part during the deposition stage. In the cooling phase, Cu atoms in the alloy body phase can inhibit excessive precipitation of carbon atoms, thus ensuring the uniform growth of graphene films on the substrate surface. As mentioned above, the preparation of graphene film by surface alloying is to better regulate the thickness of graphene film. Meanwhile, the growth of graphene film on the surface of Cu-Ni alloy substrate has better crystalline quality and integrity. However, the carbon atoms trapped in Cu-Ni substrate are a concern. When the wet chemical method is used to transfer the graphene film, as the substrate corrodes, these carbon atoms will be adsorbed to the surface of the graphene film to form impurities, thus affecting the quality of the graphene film. Therefore, we made the first improvement to the process: the diffusion depth of Ni atoms is reduced by reducing the CVD annealing time for Ni/Cu substrate. However, as shown in Fig. 9a(b) the reduction of annealing time will limit the depth and uniformity of Ni atoms diffusion, the dispersion of Ni atoms in the Cu substrate will not uniform. This will affect the uniformity and integrity of graphene growth. In this case, the part with more concentrated Ni atoms in the substrate will dissolve out more carbon atoms and eventually make the graphene film unable to grow evenly during the cooling process. Fig. 9c shows the AFM image of graphene sample corresponding the case. Due to the uneven diffusion of Ni atoms in the substrate phase, made the catalytic effect on the substrate surface is not uniform enough. It can be seen that an obvious
accumulation phenomenon occurs when carbon atoms dissolve out of the substrate surface in the cooling process.

For further improvement, we improved the sputtering process by rotating the substrate in the sputtering process and by reducing the RF power to a certain extent. On the one hand, the Ni atoms can be uniformly deposited on the substrate surface; on the other hand, the cluster diameter of the Ni atoms deposited on the substrate surface can be reduced. In addition, we found that without the fast cooling process, although the diffusion depth of Ni atoms and the dissolution depth of carbon atoms were limited, when we want to achieve the uniform growth of multi-layer graphene on the substrate, there may still be the supersaturated precipitation of carbon atoms on the substrate surface, resulting in the uneven growth of multi-layer graphene films. When the Ts drops below 600 °C, the Ni lattice in the alloy phase begins to shrink and the carbon atoms cease to dissolve out, which is why the substrate temperature needs to drop rapidly from 1050 °C to 600 °C during the cooling stage. The fast cooling process prevents excessive precipitation of carbon atoms and accelerates graphene crystallization.

We not only improved the substrate from bulk alloying to surface alloying but also limited the number of carbon atoms dissolved into the substrate at the CVD deposition stage and ensured the stable and uniform growth of graphene films. For comparison, Ni/Cu substrate sputtering for 100 minutes was alloyed for 150 minutes, and then, graphene was grown on its surface with the same deposition parameters. Finally, this comparison graphene sample was obtained after natural cooling according to the
traditional way. Fig. 9b shows the AFM image of the comparison sample, and Fig. 8d shows the sample corresponding to the curve (d) in Fig. 7. These two samples were respectively transferred to the surface of the SiO$_2$/Si substrate by a wet chemical method. Compared with Fig. 9d, more defects can be found on the surface of the graphene film in Fig. 9b. We concluded that these defects were caused by carbon atom impurities adsorbed on the substrate surface during wet chemical transfer, which condensed into small clusters and finally adsorbed on the films.

4. Conclusions

A novel Cu based substrate whose surface is alloyed with Ni atoms is used to prepare high-quality graphene films. Through a series of optimization and improvement measures, the graphene films were fabricated by the CVD method on the surface of Ni@Cu substrates with different sputtering time. The thickness of graphene film was modulated by the proportion of Ni in Ni@Cu substrate. Also, the substrate rotation measure in the sputtering process and the fast cooling measure in CVD process play two crucial roles in the uniform growth of graphene films. Finally, compared with conventional graphene films grown on Cu-Ni alloy substrates, the graphene films prepared in this study have a higher quality when transferred to other substrates by wet chemical method. A growth mechanism of thickness regulation method was proposed to explain the growth of the graphene film by using this technique, and this approach is expected to realize a controllable and reliable high-quality growth of large-area graphene films.

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References


Figure captions

**Fig. 1.** a) Fast cooling curve. b) Three different cooling method with each specific cooling rate at the different cooling stages. c) Illustration of the CVD system.

**Fig. 2.** The Raman spectrum of graphene films grown under three different cooling rates.
Fig. 3. The high-resolution image of Ni/Cu substrates with different sputtering time: a) 25 min. b) 50 min. c) 75 min. d) 100 min.
**Fig. 4.** The SEM image of Ni/Cu substrates before the CVD process, but sputtered for different periods: a) 25 min, b) 50 min, c) 75 min, d) 100 min. The SEM image of Ni/Cu substrates after the CVD alloying process: e) 25 min, f) 50 min, g) 75 min, h) 100 min. i) XRD curves of different Ni/Cu substrates. j) The peak shifts of the (200) peak.
**Fig. 5.** The EDS characterization of different Ni@Cu substrates: a) EDS spectra; b) The atomic percentage of Ni on different samples.

**Fig. 6.** a) Raman spectrum of monolayer graphene film prepared on a pure Cu substrate. b) TEM image and SAED characterization of monolayer graphene film.
Fig. 7. Raman spectra of graphene films on different Ni@Cu substrates, which were sputtered for: a) 25 min, b) 50 min, c) 75 min, d) 100 min.
Fig. 8. (a) Photo of Raman line scanning. (b) The Raman spectra obtained at 10 discrete points along with the line scan.
Fig. 9. a) Scheme of growth of graphene films on (a) Ni-Cu, (b) Ni/Cu, (c) Ni@Cu substrate which alloyed by CVD. AFM image of graphene films on SiO$_2$/Si substrate after the transfer process, which from b) Cu-Ni substrate, c) Ni/Cu substrate, d) Ni@Cu substrate.
**Table 1.** The calculation parameter from the Raman spectrum of graphene film on different Ni@Cu substrate.

<table>
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<tr>
<th>Sample ID</th>
<th>Sputtering time (min)</th>
<th>ID/IG</th>
<th>IG/IZD</th>
<th>FWHM&lt;sub&gt;2D&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tr>
<td>(b)</td>
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<td>0.98</td>
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<td>(c)</td>
<td>75</td>
<td>0.075</td>
<td>1.49</td>
<td>55.61</td>
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<tr>
<td>(d)</td>
<td>100</td>
<td>0.048</td>
<td>1.71</td>
<td>72.33</td>
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**Table 2.** The IG/I<sub>2D</sub> value at different points during Raman line-scanning.

<table>
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<td>1.2</td>
<td>1.4</td>
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<td>1.2</td>
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