Nucleation Sites for Multilayer Graphene on Nickel Catalyst

Eugene Zakar, Barbara M. Nichols, Stephen Kilpatrick, Gregory Meissner, Richard Fu, Kevin Hauri
Sensors & Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, MD, 20783
Email: eugene.zakar@us.army.mil

Abstract — The structural quality of graphene films is of immense importance both in improving growth procedures and understanding the resulting films’ electronic properties. The graphene film needs to be atomically smooth with low defects, low roughness, and high electronic mobility for high performance Field Effect Transistor (FET) devices. Because of graphene’s high optical transmittance and conductivity, it is also being considered as a transparent conductive electrode [1].

Multilayer graphene prepared by diluted methane-based CVD at 1 atm on nickel (Ni) films deposited over Si/SiO₂ wafers has been shown in various colours, sizes, and shapes [2]. Their preferred nucleation sites in relation to the Ni grain boundaries are not well understood. In this study, we prepared a variety of Ni templates having grain structures ranging from small to large and with mixed distribution across the surface. This was achieved through evaporation and sputter deposition methods. We found the greatest variety of Ni grains was achieved by changing the sputter deposition temperature (100 and 250 °C), and pressure (2 and 20 mT). The ability to grow single- and few-layer graphene on top of the Ni catalyst depended on the highly diluted methane gas in CVD, as confirmed by micro-Raman spectroscopy. Methane ratios from 0.5 vol.% to 0.41 vol.% exhibited a strong presence of graphene, 0.36 vol.% produced mixed results, and 0.24 vol.% or less produced no evidence of graphene on a Ni template after the anneal and CVD. Annealing temperatures with as small as a 25 °C difference had a great influence on final size of graphene. The grains grew almost double in size when annealed at 975 °C as compared to 950 °C. So it is advantageous to perform annealing followed by growth at the highest possible temperature and then combine it with an optimized cooling rate.

Index Terms – Graphene growth, Ni grain, morphology.

I. INTRODUCTION

Several popular techniques have been used to prepare Ni catalysts including foil, evaporation, and sputtering methods. Here we directly compare two of the prevailing deposition methods, evaporation and sputtering. Sputtering affords the widest variety of parameters to modify the growth conditions of the Ni grain size and its distribution. An extremely wide variety of grain structures were prepared to study the effects of graphene growth patterns. We show direct implication on nucleation sites for multilayer graphene on nickel catalyst.

We have also significantly diluted the mixture of methane to less than generally found 2-16 vol. % [2-5, 26]. Other studies using less than 2% vol. % [6,7,8] have shown diluted methane was key to the growth of single- and bilayer graphene and FLG (less than five layers), while using concentrated methane led to the growth of multilayer graphene that resembled bulk graphite. We employed diluted amounts equal to and below 0.5 vol. %.

II. EXPERIMENTAL ANALYSIS

A. Ni film deposition stage

A direct comparison of the Ni film deposition methods reveals changing grain structures ranging from small to large and with mixed distribution across the surface in figure 1.

Fig. 1  AFM image of Ni morphology before CVD growth of graphene by method of (a) evaporation, (b) sputtering 2 mT, 100 °C, (c) sputtering 20 mT, 100 °C, and (d) sputtering 2 mT, 250 °C.

The evaporated film grain size in figure 1a is approximately 45 nm and equilateral with an average
roughness value \(Ra\) of 8.7 nm. The grain distribution is mostly equal all around. Evaporated and sputtered thin films deposited in a condition of super saturation typically result in small grain sizes due to a high rate of nucleation \([9]\). Sputtered film grains deposited at increased temperature (100 °C) and low pressure (2 mT) grow to approximately 90 nm in size with a \(Ra\) of 9.3 nm. Sputtering above ambient temperature produces larger grain size and more defined grain boundaries than evaporated grains, as shown in figure 1b. The distribution is 30% occupancy of large grains. An increase in sputtering pressure to 20 mT tends to reduce the grain size to approximately 80 nm and reduce the occupancy to 50% large grains, as shown in figure 1c. We note the sputter deposition rate is only 43 nm/min at 20 mT almost half that deposited at 2 mT. At 20 mT, sputtering there is a reduction in free mean path of Ar atoms to the Ni target, which produces increased collisions that slow down the deposition rate. An increase in the sputter temperature to 250 °C produces noticeably larger grains of roughly 600 nm in size with a \(Ra\) of 27 nm, as shown in figure 1c. At this temperature, there is evidence of grain growth and formation of large flat plateaus from topographical features (figure 1d).

**B. Ni annealing stage**

After 20 min of annealing at 975 °C, the average grain size increase to several times its original size. If we compare how the grains evolve from their original size in figures 1a to 1c and their corresponding annealed state figure 2a to 2c, we find the distribution remains nearly the same mix. That is, the proportion of small grains and large grains are relatively the same. In evaporated films, the grains continue to be equilateral and grow to an average size of 2000 nm, which is an approximately 50 times increase from their original deposited condition.

![Figure 2](image.jpg)

**Fig. 2** Morphology of (a) equilateral grains from evaporation; (b) 30% large grain from sputtering, 2 mT and 100 °C; and (c) 50% large grains from sputtering, 20 mT and 100 °C.

The sputter deposited grains reach a maximum 10,000 nm in size, nearly 11 times their original size. Other investigators have shown on average a 20 times increase in growth \([10]\). The large grains occupy 30% of the surface when sputtering pressure is held at 2 mT, but occupy 50% when the pressure is 20 mT. The effect of increasing the sputter pressure was to suppress the nucleation of small grains around larger grains.

The results for sputtered film at temperature elevation of 250 °C (figure 1d) are not shown here, but for 450 °C the final grain size is said to approach 25 µm after the annealing stage \([11]\). Grain growth will stagnate in thin films during annealing at some point according to the film thickness.

The ratio of the annealed grain diameter to that of the nickel film is generally said to be around 20, which could only be obtained by abnormal grain growth \([12]\). Normal grain growth rarely occurs in thin films. An important characteristic of the normal grain growth is that, after the annealing, the average grain size does not exceed the original film thickness. The shape and grain size distribution of the single grain does not change. Abnormal grain growth is preferred because the average grain size can be up to an order of magnitude larger than the original film’s thickness. Others have shown greater than normal Ni grain diameter growth to 50 µm by exposing the film to a pressurized vessel of 200 Torr at 1000 °C and extending the annealing time from 20 to 60 min \([6]\), but there was no mention of the quality of surface roughness resulting from this process.

**C. Graphene growing stage**

A source of carbon in the CVD process for the growth of graphene on top of the Ni catalyst is due to the reaction product from gas mixture of \(H_2\) and \(CH_4\) at 975 °C in atmospheric conditions \([13]\). Since the solubility of carbon in Ni is temperature-dependent, carbon atoms segregate as a graphene layer on the Ni surface upon cooling. Others \([14]\) have used thin Ni films (700 nm, deposited by sputtering on \(SiO_2/Si\) wafer) rather than thick Ni foil (0.5 mm) to minimize the saturation time and the amount of carbon in the Ni film, since the solubility of C in Ni is about 0.9 at. % at 900 °C. For other materials, like Cu, the carbon solubility is negligible and the substrate can reach a substrate thickness of 25 µm. For Ni, we used a thin-film layer of 300 nm.

Finding evidence of graphene growth can sometimes be challenging naked eye. Single- or bilayer graphene are transparent \([15]\), but multiple layers of crystallites are opaque and can be visualized using optical microscopy. Visual detection of single- and bilayer graphene is improved by transferred graphene to any 300-nm-thick \(SiO_2\) substrate and using monochromatic illumination \([16]\). The apparent transparency of 1-3 layer graphene grown over the Ni catalyst is beneficial for determining the background surfaces. The morphology and grains of the Ni are discernible in figure 3. The black lines are the Ni grain boundaries and the graphene patches represent several layers. The grain boundaries of Ni at the CVD stage take on the same fingerprint characteristics as compared to the annealing stage.

![Figure 3](image.jpg)

**Fig. 3** Distribution of graphene patches on top of (a) evaporated Ni with equilateral grains; (b) occupancy 30% large grains from sputtered, 2 mT and 100 °C; and (c) occupancy 50% large grains from sputtered, 20 mT and 100 °C deposit conditions.
Inspection of the grain boundaries after graphene growth reveals the preferred nucleation sites of multilayer graphene patches. In figure 3a, graphene patches measuring approximately 10 µm across appear to cover several smaller grains of Ni prepared by evaporation method. When a Ni grain diameter is relatively large from a sputter preparation method, as depicted in figure 3b, the graphene patches prefer to grow in concentrated areas of small Ni grain boundaries and are less likely to appear on top as single large flat areas. There is a higher density of atomic steps due to the curvature of the grain edge, thereby inducing the nucleation sites of graphene patches [2,10]. In areas depicting large equilateral grain size with fewer grain boundaries, such as in figure 3c, the quantity of graphene patches appears to remain relatively unchanged compared to figure 3a.

It appears that long length grain boundaries can have few nucleation sites, and on the other hand, short length grain boundaries can have many nucleation sites. If multilayer graphene originates at the grain boundaries, as seen in both figures 3a and 3b, then hypothetically the large numbers of grain boundaries in figure 3a should be completely covered of multilayer graphene patches. One possible reason for the few nucleated multi-graphene sites on overwhelming numbers of Ni grains boundaries is that the individual grains have a (111), (100), and possibly more crystallographic orientation [5]. In face-centered cubic (fcc) metals such as Ni, the (111) planes have their lowest surface/interface energy with respect to other planes [9] and growth is preferred in those planes. However, in Ni films that have high stress, the surface/interface energy minimization is no longer the dominant driving force. Ni grains growth is preferred with a (100) crystallographic orientation because Young’s modulus allows the grains to expand and contract in those planes much more easily in order to reduce the internal stress. Usually high quality epitaxial grown graphene is associated with the smallest lattice mismatch, but this tendency needs to be studied further before making a concrete determination. The driving force or nucleation sites of multilayer graphene patches are not strongly dependent on grain size when using diluted methane concentrations below 0.5 vol. %.

A stronger influence of the quality and quantity of graphene is dictated by the effect of temperature and the rate of cooling at diluted amounts of methane. Other studies have shown a moderate cooling rate provides the best conditions for graphene growth [8]. At moderate cooling rate, C atoms segregate and form graphene; while at a higher rate, C atoms segregate out of Ni, but form a less crystalline, defective graphitic structure [17]. Others have used very fast cooling rates of 10 °C/sec successfully, but these conditions were done with either thicker films or higher concentration (5-16 vol %) of methane [3,4,15] and high (400 Torr) pressure [5]. We chose a slow cooling rate of 5 °C/min for our thin-film Ni and a dilute methane concentration.

The CVD temperature also has a strong influence on the graphene patch size. We lowered the process temperature to 950 °C to determine the change in graphene patch size. When the temperature was reduced by 25 °C from the original condition (figure 4a), the graphene patches were reduced to nearly half the size (figure 4b) for the evaporated sample. The largest size graphene patch at 975 °C measured 20 µm across for a 300-nm thickness Ni film.

A methane ratio from 0.5 to 0.41 vol. % exhibited a strong presence of graphene film, at 0.36 vol. % produced mixed results, and at 0.24 vol. % or less produced no evidence of graphene on a Ni catalyst after CVD. We were successful in growing graphene with mixed results below 0.36 vol. % by extending the CVD growth time to 10 minutes from the previous 5 min [6]. It is expected that conditions such as annealing time, temperature, and hydrogen content will shift these results.

The hydrogen environment plays an important role in preventing oxidation of Ni at high temperature. The quality of the film has been shown to improve with the addition of hydrogen [18]. The likely explanation for this is that hydrogen is known to selectively etch amorphous carbon defects that can serve as secondary nuclei for competing film growth. It can also cause problems to thin-film Ni and other metals over time or if the content is too high, in a phenomenon called hydrogen blistering [11]. Pinholes are shown in figure 3c in the form of tiny black holes, which can vary in size and density with the amount of hydrogen flow in the process. At elevated temperatures, hydrogen atoms are able to diffuse into Ni and accumulate in clusters until the pressure builds up to the point of bursting. Reducing the amount of H₂ during the annealing stage is important in preventing pinholes in very thin Ni films. We are in the process of quantifying the number of defects versus the H₂ content and will report on this at a later time, as this can have tremendous consequences on the yield of FET devices production from a thin-film Ni catalyst. On a very thick Ni film (0.5 mm), a 1-hour H₂ anneal prior to CVD was reported necessary to achieve successful growth graphene [2], but there was no mention of the post surface roughness conditions.

### C. Raman Spectroscopy

The amount of graphene layers segregated on the Ni catalyst surface after CVD growth can be characterized by
Raman intensity peaks. Figure 5 shows a comparison of graphene grown patches on the Ni surface ranging from light to dark shades of gray.

![Fig. 5 Comparison of images according to (a) clear or transparent, (b) light, (c) medium, and (d) dark graphene patches on evaporated Ni surface.](image)

Micro-Raman spectroscopy was positioned at the crosshair locations corresponding to those same images and the intensity peaks are recorded in Figure 6.

![Fig. 6 Comparison of Raman intensity peaks according to (a) clear or transparent, (b) light, (c) medium, and (d) dark graphene patches on Ni.](image)

Raman bands at 1580 to 1584 cm\(^{-1}\) and 2711 to 2713 cm\(^{-1}\) are denoted as the G band and 2D band, respectively [25]. The 2D band is also denoted as G’ band in some work [27]. Differences among the Raman spectra were observed, including an increase of the G band to 2D band intensity ratio and a broadening of the 2D band. The G band originates from in-plane vibration of sp2-hybridized carbon atoms and generally becomes stronger with an increasing number of layers, for layers typically smaller than 10. The 2D band becomes broader and shifts toward a higher wave number with increased graphene layers due to a splitting of the electronic band structure. Figure 6 shows Raman spectra of different number of graphene layers, exhibiting the G and 2D modes. The intensity ratio of G to 2D modes increases with the number of graphene layers. Single-layer graphene typically has a sharp and symmetric 2D band at 2683 cm\(^{-1}\) depending on the background substrate [19, 20], but we see no evidence of this in the chart. Where two or more layers of graphene exist, the shape of the 2D mode evolves significantly. The 2D mode in bulk highly ordered pyrolytic graphite (HOPG) generally can be resolved into two components, 2D\(_1\) and 2D\(_2\), where as single-layer graphene has a single sharp component [21]. Single 2D component, monolayer, and four components in bilayer have been explained in terms of double resonance Raman scattering [22]. The 2D\(_1\) component is less intense than the 2D\(_2\) component; whereas, for the bilayer these bands have almost the same intensity. An increase in number of layers leads to an incremental increase of the higher frequency 2D\(_2\) component compared to the 2D\(_1\) component. These characteristics of a bilayer are present in figure 6a with broadening of the 2D band centralizing near 2700 cm\(^{-1}\) and the I(G)/I(2D) ratio near unity. The Lorentzian 2D curve is symmetrical, although missing is a typical hump on the left hand side, normally associated with two-layer graphene [23]. Multilayer graphene exists when the I(G)/I(2D) ratio increases in the range above two layers with the broad shape of the 2D mode becoming asymmetrical and shifting to higher wave numbers, as shown in figures 6b, 6c, and 6d. The Raman spectra show very similar characteristic of trilayer graphene. High resolution Raman spectra and micrographs similar to figures 3 and 4 after the transfer process also confirm the growth of large-area single- and bilayer graphene by controlled carbon precipitation on polycrystalline Ni surfaces [8]. The intensity of the G band increases almost linearly as the graphene thickness increases [19]. All the layers show activity at the 1340 cm\(^{-1}\), also known as the D band, which relates to the occurrence of defects and disorder in the crystal. The disorder-induced D bands at the 1355 cm\(^{-1}\) became distinct for thinner graphene films, a reflection of how defects can be easily be incorporated into thinner graphene sheets [26]. The relative intensity of an existing D band decreasing to less than 10% of the G band with increasing crystallite graphene layers is comparable to high-quality graphene films grown by CVD [24]. We are in process of transferring the graphene layers to SiO\(_2\) substrates to improve the Raman resolution and also reduce the laser intensity that can possibly damage the graphene.

### III. Conclusions

Multilayer graphene patches are not dependent on the grain size of the Ni catalyst when the diluted methane concentration is equal to or below 0.5 vol. %. This was demonstrated by growing Ni films with a variety of grain sizes via evaporation and sputtering methods followed by a CVD of graphene. Multilayer graphene patches were distributed equally onto the surface regardless of changing grain sizes. The process temperature had a strong influence on the size of graphene patches. A 25 °C change in CVD temperature can be used to change the size of multilayer graphene by almost a factor of two, particularly on evaporated Ni. Annealing at the highest possible temperature and combining it with an appropriate cooling rate results in the largest possible multilayer graphene patch size. The surface of the Ni catalyst after CVD with diluted methane is made of trilayer graphene with multilayer patches. We are investigating the role of hydrogen in the CVD process to determine the quality and quantity of defects on the surface of both sputtered and evaporated Ni catalyst. Evaporation and sputtering methods offer a wide variety of morphologies in Ni catalysts to study the structural quality of graphene films.
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