

Synthesis of High Quality Graphene Using Diamond-Like Carbon (DLC) as Solid Carbon Source

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ABSTRACT

We report the first demonstration of synthesis of high quality graphene using Diamond-Like Carbon (DLC) as solid carbon source. Graphene are formed on samples with different structures after high temperature annealing and subsequent cooling down. New sample structures are used first time in this work. High quality single layer/bilayer graphene Raman spectra are obtained. It is demonstrated that DLC thickness, nickel thickness, SiO₂ capping layer and annealing temperature have influences on the final graphene quality.

1. INTRODUCTION

Due to its unusual transport properties [1], graphene has been attracting significant research efforts ever since its first isolation in the year of 2004 [2]. Graphene is considered as a potential successor of Silicon (Si) for future nanoelectronic applications. Several approaches have been proposed and studied for large scale graphene formations which aim to meet the challenge of device application, including thermal decomposition of Silicon Carbide (SiC) [3],[4] and chemical vapor deposition (CVD) on nickel (Ni)/copper (Cu) layers [5],[6]. Most recently, syntheses of graphene using solid carbon source were reported [7],[8]. The method of using solid carbon source has its unique advantages such as precise control of the amount of carbon involved in the graphene formation process, as compared with other approaches.

In this paper, we report the first demonstration of synthesis of graphene using high sp³ containing DLC film as solid carbon source. High quality single layer/bilayer graphene Raman signatures are obtained using this approach. The impacts of SiO₂ capping layer, as well as Ni thickness t_{Ni} , DLC thickness t_{DLC} , and temperature, are explored.

2. EXPERIMENTAL DETAILS

Fig. 1 (a)-(c) illustrate the three sample structures used in this work. Si wafers with 400 nm field oxide (FOX) were used as starting substrates. For structure A, a DLC layer was deposited first using a Filtered Cathodic Arc (FCV) system, followed by depositions of a Ni layer (magnetron sputter system) and a SiO₂ capping layer (e-beam evaporator). For structure B and C, Ni layers were deposited before DLC layers. Structure C has an additional SiO₂ capping layer as compared with structure B. Structure B and C are used for the first time in graphene synthesis process using solid carbon source. Samples with different t_{Ni} and t_{DLC} were prepared to explore t_{Ni} and t_{DLC} effects on graphene quality. After sample preparation, all samples were subjected to high temperature annealing in a Rapid Thermal Annealing (RTA) system, followed by cooling down to room temperature. Graphene was formed during the cooling down process, which is attributed to the temperature-dependent solid solubility of carbon in Ni. Optical Microscopy (OM), SEM, TEM, and Raman Spectroscopy were used to characterize the graphene samples in this work.

3. RESULTS AND DISCUSSION

Fig. 1 (d) is the Raman spectrum of one 10 nm as deposited DLC layer. The spectrum shows high sp³ content in the original DLC film.

Raman spectra of graphene formed on two samples which are both with sample structure A but different t_{Ni} are shown in Fig. 2.

The ratio of t_{Ni} to t_{DLC} was kept the same (1:2) for the two samples. Both samples were annealed at 1000 °C for 120 s and cooled down. Fig. 2 demonstrates that graphene can be formed using DLC as solid carbon source. The sample with larger t_{Ni} shows better graphene quality, which can possibly be attributed to the better metal quality of the thicker Ni layer. The high resolution TEM image of the sample with 8 nm Ni shown in Fig. 3 further demonstrates that multi-layer graphene was formed using our method.

Samples with structure B were annealed at 1050 °C for 10 s and cooled down to form graphene. All samples are with the same t_{Ni} of 150 nm but different t_{DLC} (4 nm to 21 nm). OM and SEM images of the sample with t_{DLC} of 4 nm are shown in Fig. 4 (a) and (b), demonstrating partial graphene coverage. This is due to the insufficient carbon atoms in this sample. Fig. 4 (c) and (d) show full graphene coverage on the annealed sample which was deposited with a thicker DLC of 7 nm. Fig. 5 demonstrates the Raman spectra of Point 1 and 2 on the sample with 4 nm t_{DLC} , further illustrating that the region where Point 1 is in is covered with graphene, while that of Point 2 is not. Fig. 6 shows the typical Raman spectra of graphene formed by samples different t_{DLC} . It can be observed that the typical Raman spectrum of graphene formed on the sample with 7 nm DLC has the single layer or bilayer graphene Raman signatures while the rest are with multi-layer signatures, demonstrating that appropriate t_{DLC} facilitates single layer/bilayer continuous graphene formation.

The OM images of graphene developed from samples with 9nm DLC + 200 nm Ni (sample 1, structure B) and 10 nm SiO₂ + 9 nm DLC + 200 nm Ni (sample 2, structure C) are shown in Fig. 7 (a) and (c), respectively. Fig. 7 (b) and (d) are the corresponding SEM images of the former and the later. It can be observed that the pinhole formation on the sample surface was significantly reduced in sample 2, which is due to the SiO₂ capping layer. Fig. 7 (e) and (f) are the OM and SEM images of graphene formed on the sample with 10 nm SiO₂ + 9 nm DLC + 200 nm Ni which was annealed at 900 °C for 120 s (sample 3). Based on SEM images, the graphene grain size in sample 2 is larger than that in sample 3. Fig. 7 (g) and (h) are the AFM images of sample 2 and 3. Significant surface profile differences can be observed between these two. Fig. 8 shows the Raman spectra of three typical points from these two samples. Higher graphene quality, which is better than reported before [7],[8], was observed on sample 2.

5. CONCLUSION

The synthesis of high quality graphene using DLC as carbon source was reported for the first time. New sample structures were used in this work. Using DLC as solid carbon source and SiO₂ capping layer to form graphene has its unique advantage of reducing pinhole formation. DLC thickness, Ni thickness, and temperature effects on graphene quality were also discussed.

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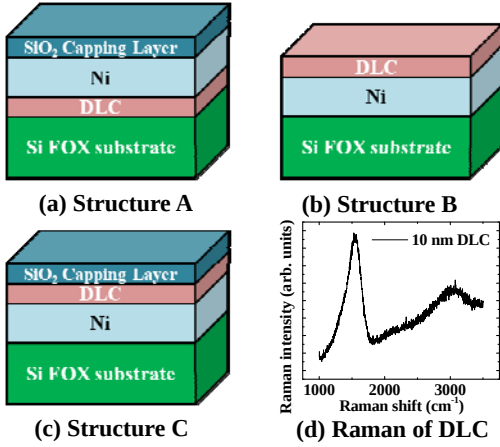


Fig. 1. (a), (b), and (c) are sample structures used in this work to form graphene. Structure A is with carbon source under Ni layer, while structure B and C are with DLC on top of Ni; (d) Raman (wavelength 514 nm) spectrum of 10 nm as deposited DLC layer on Ni.

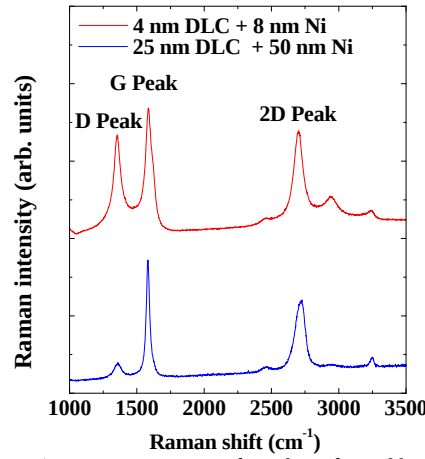


Fig. 2. Raman spectra of graphene formed by samples with the same structure (structure A) but different DLC and Ni thickness. Sample with thicker Ni layer shows better graphene quality.

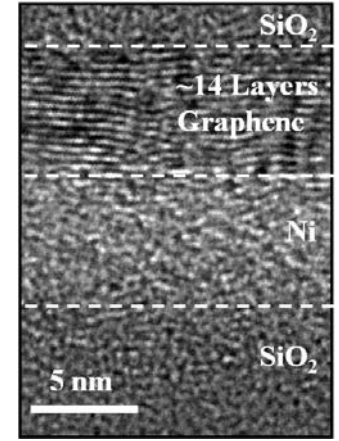


Fig. 3. High resolution TEM image of a multi-layer graphene sample. The starting sample was with 4 nm DLC and 8 nm Ni.

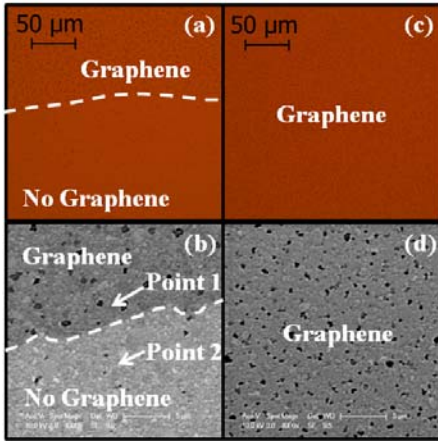


Fig. 4. (a) OM and SEM images of graphene formed by samples with 4 nm DLC + 150 nm Ni ((a) and (b)), and 7 nm DLC + 150 nm Ni ((c) and (d)). DLC layers were deposited first before Ni layers (structure B) during sample preparations.

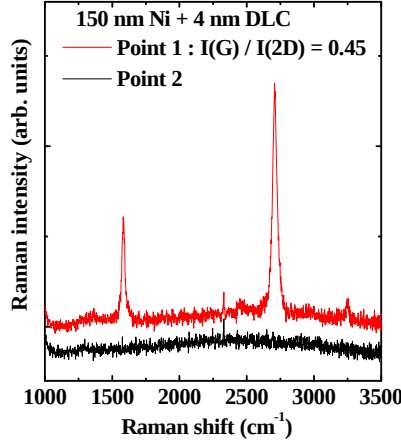


Fig. 5. Raman spectra of Point 1 and 2 in Fig. 4 (b). Point 1 shows single layer/bilayer graphene Raman spectrum (The ratio of the G and 2D peak strength, $I(G)/I(2D)$, is 0.45), while point 2 has no graphene signal.

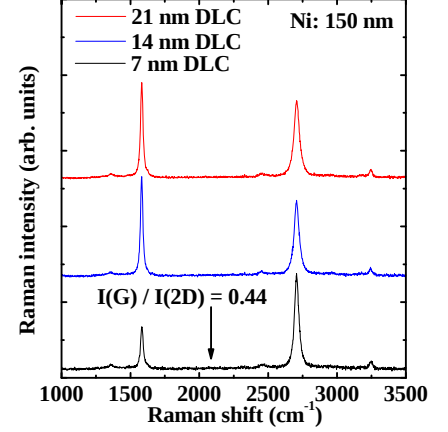


Fig. 6. Typical Raman spectra of graphene formed by samples with the same Ni thickness (150 nm) but different DLC thickness. Appropriate DLC thickness facilitates single layer/bilayer graphene formation.

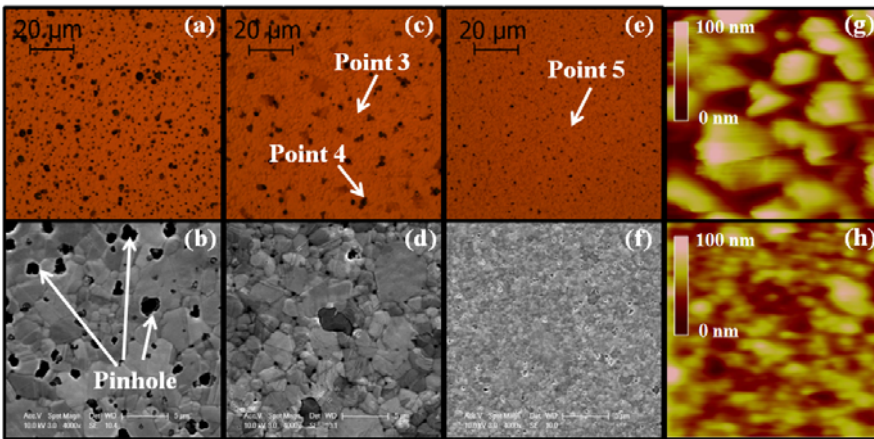


Fig. 7. (a), (c), and (e) and (f) are the OM images of graphene developed from sample 1 (9nm DLC + 200 nm Ni, annealed at 1050 °C for 10 s), 2 (10 nm SiO₂ + 9 nm DLC + 200 nm Ni, annealed at 1050 °C for 10 s) and 3 (10 nm SiO₂ + 9 nm DLC + 200 nm Ni, annealed at 900 °C for 120 s). (b), (d), and (f) are the corresponding SEM images. Sample 1 was with structure B, and sample 2 and 3 were with structure C, before graphene formations. Pinhole formation was significantly surmounted in sample 2 in comparison with sample 1, which is attributed to SiO₂ capping layer. Larger graphene grain size can be observed in (d) as compared with (f). (g) and (h) are the AFM (tapping mode) images of sample 2 and 3, further demonstrating sample 2 has larger graphene grain size than sample 3.

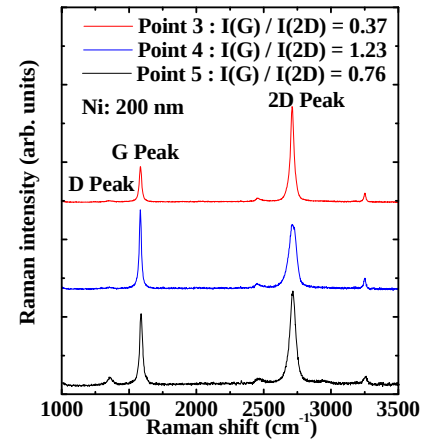


Fig. 8. Raman spectra of Point 3 and 4 in Fig. 7 (c) and Point 5 in Fig. 7 (e). Graphene quality formed by 1050 °C annealing is typically better than that by 900 °C annealing. Very small D peak to G peak ratio was observed on Raman spectrum of Point 3 and 4. $I(G)/I(2D) = 0.37$ and 1.23 for Point 3 and 4, respectively.