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Shailesh Kumar
Trinity College Dublin

N McEvoy
Trinity College Dublin

T. Lutz
Trinity College Dublin

G. Keeley
Trinity College Dublin

Nicholas Whiteside
University of Wollongong, njw795@uowmail.edu.au

See next page for additional authors

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Abstract

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Keywords

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Authors

Shailesh Kumar, N McEvoy, T. Lutz, G. Keeley, Nicholas Whiteside, Werner Blau, and G. Duesberg

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Low Temperature Graphene Growth

S. Kumar[a,b], N. McEvoy[a,c], T. Lutz[a], G. P. Keeley[a,b], N. Whiteside[a,d], W. Blau[a,c] and G. S. Duesberg[a,b]

[a] Centre for Research on Adaptive Nanostructures and Nanodevices, Trinity College Dublin, Dublin 2, Ireland
[b] School of Chemistry, Trinity College Dublin, Dublin 2, Ireland
[c] School of Physics, Trinity College Dublin, Dublin 2, Ireland
[d] University of Wollongong, Wollongong, NSW 2522, Australia

We demonstrate the growth of graphene films on nickel substrates by chemical vapour deposition using acetylene at temperatures as low as 750 ^{O}C, opening a viable route for its scalable production. Raman spectroscopy was used to confirm defect-free mono and multilayer graphene at and above this temperature, and of defective graphene at lower temperatures. Atomic force microscopy and scanning electron microscopy performed directly on the films give an indication of graphene flake size, morphology and also the topography on substrate.

An unexpected dependence of graphene thickness on precursor dwell time is reported. This together with low temperature growth suggests deficiencies in existing growth models and hints at a more complicated growth mechanism.

Introduction

Graphene is of huge interest to the scientific community because of its exciting electronic properties. In order to investigate the electrical properties of graphene it must be produced and patterned using scalable and reproducible methods. To date micro-mechanical cleavage (1) and epitaxial growth on SiC (2) at very high temperatures have been the principal techniques used for producing graphene. Recently, the exfoliation of graphene in organic solvents (3) and water surfactant solutions (4) has been reported which results in a major improvement in terms of the graphene manufacturability. However, for looking towards applications and large scale fabrication graphene synthesis with methods such as chemical vapour deposition (CVD) is most desirable.

CVD type graphene formation on Ni <111> surfaces was proposed several years ago in steam reforming processes (5). The graphene formation is proposed to take place at steps on the Ni surface, similar to what has been observed in the formation of graphitic fibers and nanotubes (6,7). Another mechanism for graphene formation on metallic substrates including Ru (8) and Ir (9) has been reported recently. It relies on the temperature dependent solubility of carbon in metals. In this method, carbon is dissolved in metal at high temperatures (generally above 1000°C) and then segregates on to the surface of the metal as temperature is lowered. Nickel (Ni) is particularly suited for such growth since it's <111> face matches the surface lattice almost perfectly with graphene and also it has a higher solubility for carbon than the above metals (10, 11). Indeed, several authors (12, 13, 14) have applied this mechanism to grow graphene on Ni substrates. In these works methane was decomposed at 1000°C to provide free carbon. The use of a relatively high temperature requires thick and high quality Ni films in order to avoid buckling up due to coagulation, which leads to a rough surface.

Here, we report graphene formation at temperatures as low as 750C on sputtered Ni substrates. Raman spectroscopy was used for proving the existence of mono to multilayer graphene. This finding is not only a significant step towards the manufacturability of graphene but it will also enable many new experiments by putting fewer constraints on substrates that can be used. Furthermore, an unexpected dependence of graphene thickness on precursor dwell times is reported. This and the low temperature growth hints towards a growth mechanism which is somewhat more complicated than that of simple segregation controlled growth. These observations will help to elucidate the graphene formation mechanism, providing strategies to optimise the growth.

Experimental

Nickel substrates were prepared by sputtering 300 nm Ni on 300 nm of thermally grown silicon dioxide in a Torr International sputterer. The substrates were then introduced in a tube furnace heated to temperatures between 650 ^{o}C-1000 ^{o}C. A mixture of hydrogen and argon (1:1) was then introduced for 3 minutes, allowing the samples to equilibrate to the high temperature. This annealing also results in curing of the Ni substrates. The carbon feedstock (acetylene) was then introduced keeping overall pressure at 1 Torr. This flow was maintained for various growth periods (dwell time). When quenching the growth, substrates were cooled under nitrogen flow (with cooling rate >10 ^{o}C/s) by removing the substrates from the heated zone. The cooling procedure was identical for samples prepared at different temperatures.

Raman spectra were taken with a Jobin-Yvon Labram Raman spectrometer using an excitation wavelength of 633nm, with typical spot size of the probe being 2 μm. A Hitachi 4300 FE SEM with an acceleration voltage of 2-5 kV was used for imaging the graphene layers directly on the substrates. AFM was performed on the as-grown samples using an Asylum MFP-3D AFM in tapping mode.

Results

In Fig.1 we show a typical SEM image of a sample surface after CVD growth at 950^{o}C. The samples show Ni crystallites in the range of 1 to 2 μm. These form during the annealing period and are smaller than those reported by other authors (13, 14). We have used sputtered Ni, which generally gives rougher films when compared to thermal and E-beam evaporation which was used by the noted authors. The nickel crystallite determines the regions for homogenous graphene formation (15), which was confirmed by our Raman investigations. The contrast of the SEM image indicates flakes of varying thickness and suggests good surface coverage with carbon. In Fig.1 the bright spots are Ni blobs protruding from underneath the graphene layers shown by darker shades.

An AFM image of the substrate grown at 950°C is shown in Fig 2. The surface exhibits granular structures with height differences up to 40 nm, with grains widths in the order of micrometers – as observed in the SEM. The surface roughness within a grain is very small. In Fig 2 (right) an AFM image of a sputtered Ni film for graphene formation is shown. It has a high surface roughness due to its granular morphology, which is reduced considerably due to crystallite growth during the annealing procedure.

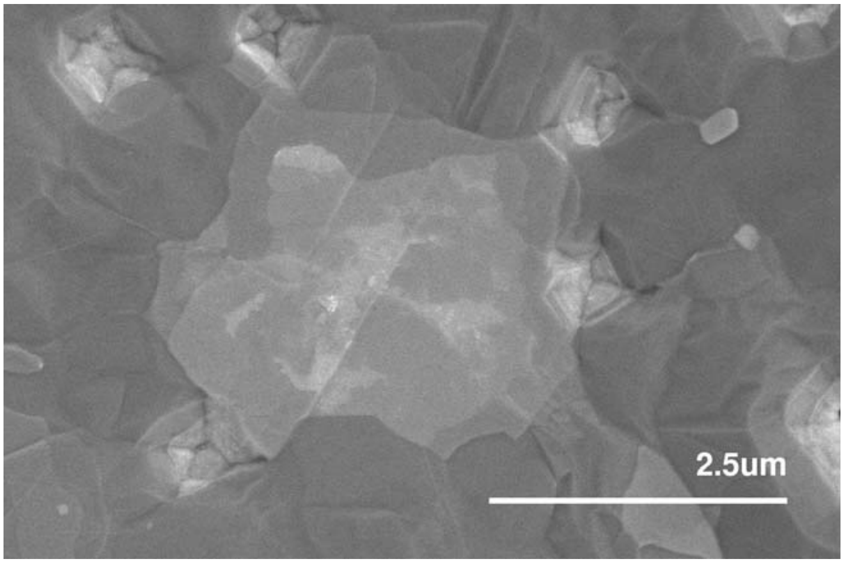

Figure 1. SEM image showing grains of Ni and graphene flakes deposited on it.

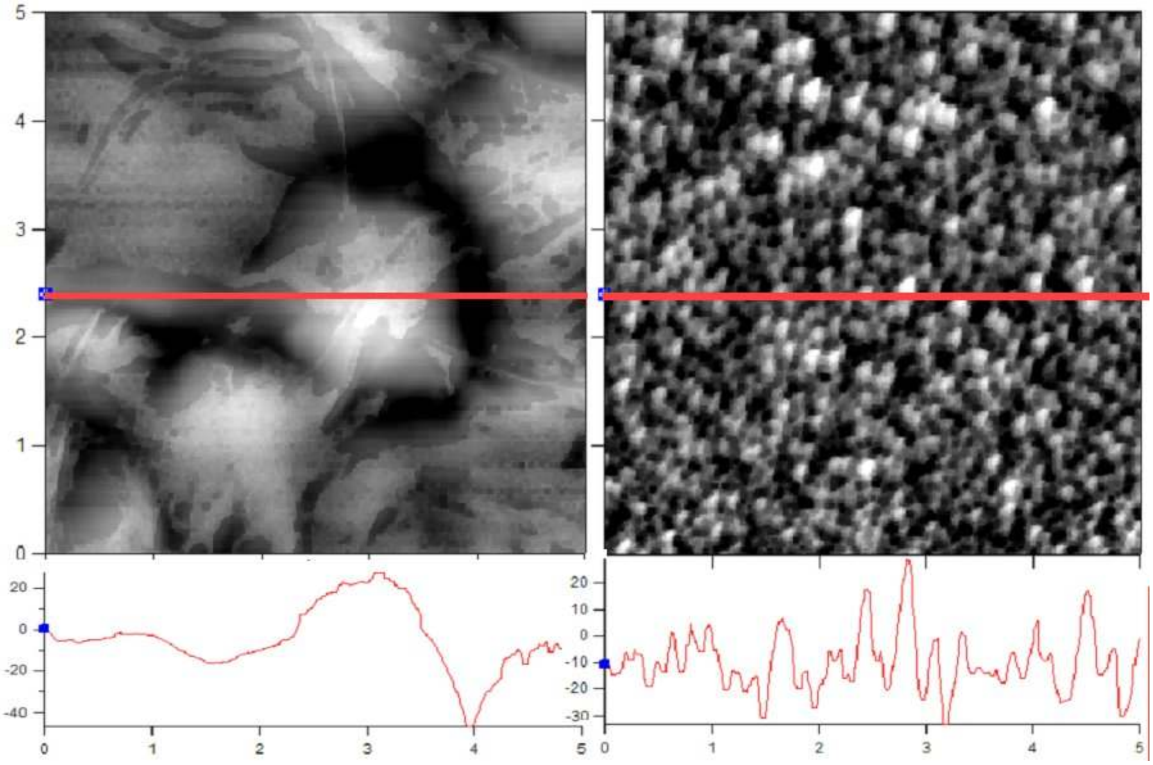

Figure 2. AFM image (5 µm × 5 µm) of sample grown at 950°C (left), and same sample with Ni as sputtered. Lower portions show height sections along the red lines (in nm).

Typical Raman spectra of samples grown at 950 °C are shown in Fig.3. The most dominant features in these spectra are the 2D peak at 2665cm^{-1} and the G peak at 1584 cm^{-1}. Most regions on samples produce spectra similar to 1(a), but those similar to

1(b) are also seen. The linewidth of the Lorentzian 2D peak is about 40 cm^{-1} for spectrum 1(a), while it's less than 30 cm^{-1} for 1(b). The 2D/G ratio is about 1 for spectrum 1(a) and 3.5 for spectrum 1(b). The spectra do not exhibit any D peak (normally occurring at about 1380 cm^{-1}), which indicates the absence of defects and therefore perfect crystalline order.

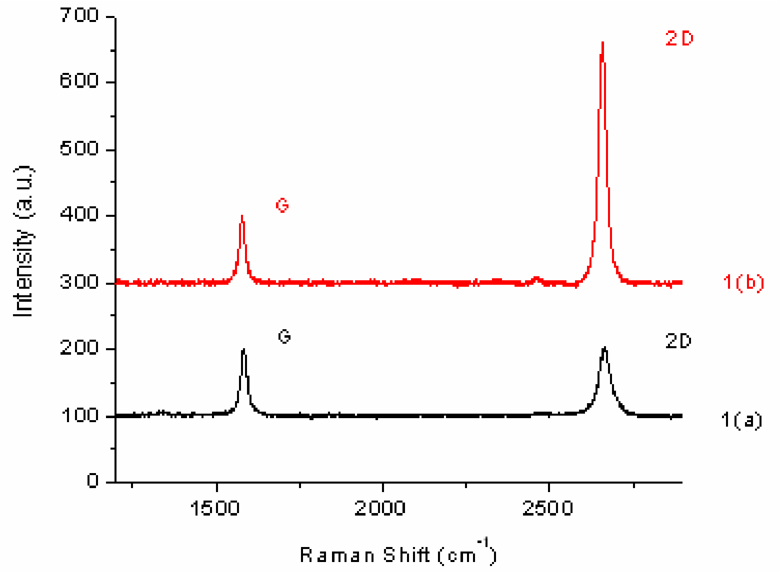

Figure 3. Raman spectra of samples grown at 950^{o}C. On a typical sample spectra like 1(a) occur more frequently than spectra with high 2D/G ratios like 1(b).

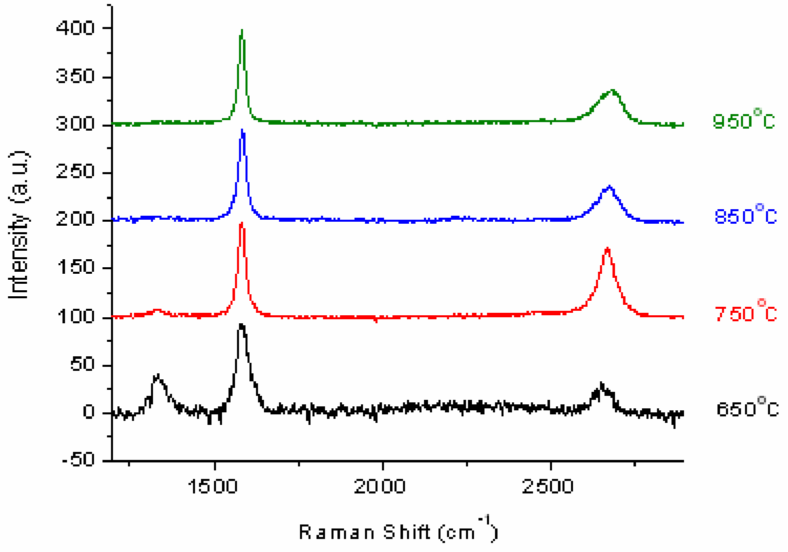

Figure 4. Raman spectra of samples grown at different temperatures.

In Fig.4 we show the Raman spectra of samples grown at different temperatures. The 2D/G ratio for spectra are 0.4 (650^{o}C), 0.7 (750^{o}C), 0.37 (850^{o}C) and 0.33 (950^{o}C). The D peak can be seen increasing as the temperature decreases. The spectra taken for samples at 950 ^{o}C and 850 ^{o}C show no D peak, for the 750 ^{o}C sample a D peak starts to become noticeable and at 650 ^{o}C it becomes quite appreciable.

In another experiment we prepared a set of samples at 950 ^{o}C with different precursor dwell times. All other conditions were kept constant, including the cooling rate. The

Raman spectra of these samples with dwell times from 30s to 5 minutes are shown in Fig.5. All spectra have negligible D peaks, indicating that the graphitic depositions are highly crystalline. Apart from decreasing 2D/G ratios 0.33 (5 min), 0.48 (3 min), 0.74 (1 min) and 3.7 (30 s)), the linewidth of the 2D peak increases as the dwell time is increased.

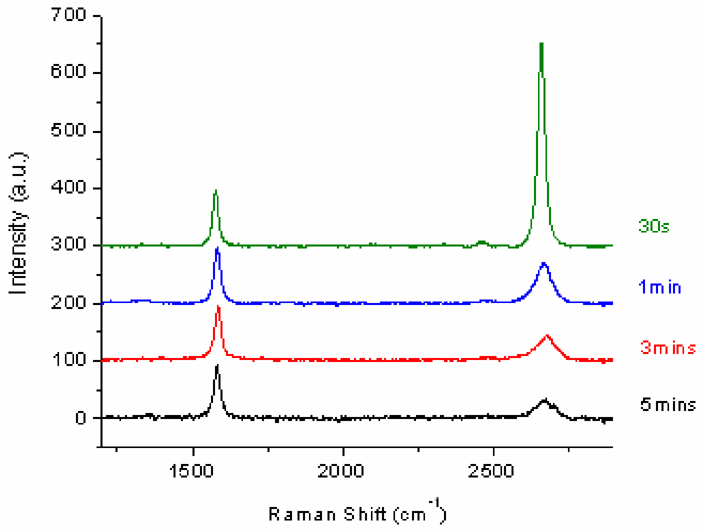

Figure 5. Raman spectra of samples grown at 950^{o}C with different dwell times.

Discussion

Our Raman data clearly shows the formation of graphene on Ni substrates. The ratio of 2D and G peaks and the linewidth of 2D peaks have been used as measure of the thickness of graphene layers. The 2D/G ratio of 3.7 and 2D linewidth of less than 30cm^{-1} obtained for spectra 1(b) in Fig.3 matches with numbers reported for monolayers of graphene grown on Ni substrates (16). The value of these quantities for spectra 1(a) indicates the presence of 2 or 3 layers of graphene. Since the majority of Raman spectra on the substrate are similar to spectrum 1(a), we conclude that bilayer or multilayer graphene covers most of the surface area of the sample. The presence of regions of monolayer graphene is proven by spectra 1(b).

The absence of D peaks in these spectra proves highly ordered graphitic deposition in the region scanned by Raman probe. Graphene flakes with sizes of about 2 µm (size of Raman probe) therefore frequently occur, since otherwise there would be significant D-line contribution from edges (17, 18). This observation is in agreement with the size of domains seen in SEM and AFM images.

We attribute the predominance of multilayer graphene in our samples to the roughness of our nickel substrate. Other authors have already noted the importance of an atomically flat nickel surface for growth of large monolayer graphene flakes. In particular, the grain boundaries and other defects result in multilayer graphene. Our substrates were sputtered and this provided a very rough surface of Ni to start with, as seen in Fig.2 (image on right). This roughness is reduced to a great extent by our annealing treatment (as seen in left image in Fig.2). This shows that easy accessible sputtered Ni films can be used for graphene growth.

The Raman spectra for growth at different temperatures show that the deposited carbon is graphitic and the defects (or disorder) in it increase as the temperature is decreased. Of particular note is the growth occurring at 750 °C since its 2D/G ratio and line shape matches closely of 3 layer graphene grown on Ni<111> at 1000 °C (16). At higher temperatures these quantities indicate a larger number of graphene layers. The spectrum for the sample grown at 650 °C although graphitic shows a larger disorder than other samples.

The current model of segregation induced growth to describe the growth of graphene on Ni hinges on the strong temperature dependence of both solubility and diffusivity of carbon in metals. Lowering the temperature produces not only a many-fold decrease in solubility, but more importantly reduces the diffusion constant exponentially. This means that almost all of the carbon gets segregated in the early part of cooling when the temperature is still high. This has been shown by Yu et al. (12) when they demonstrated that with a very high cooling rate it is possible to freeze almost all the carbon inside Ni, while monolayers of graphene were formed only at medium cooling rates. From this it would appear that low temperature growth of graphene soley by segregation is rather unlikely, since neither the low solubility of carbon nor its low diffusibility at temperatures below 800 °C should allow graphene formation. Our result of low temperature graphene formation therefore indicates a contribution of a CVD type of growth. This point is backed up by the fact that our growth conditions are similar to those of catalysed CVD growth of carbon fibers and tubes on Ni clusters.

Our results on dwell time are also not consistent with the segregation induced growth model. The 2D/G ratio of spectra shown in Fig.5 decreases as the dwell time increases. This means that the thickness of graphitic deposit tends to increase (from monolayer to 3 layers to 5-10 layers of graphene) as the dwell time of precursor is increased. This is not predicted by the segregation model, according to which, the growth is a result of cooling induced segregation of carbon from Ni, which will occur only when the cooling is applied and should therefore be independent of dwell time. This increase in average thickness of deposit with dwell time was also observed in the experiments of Kim et al. (14).

Conclusion

We have demonstrated the growth of graphene films on sputtered nickel substrates at temperatures as low as 750 °C. The simple sample preparation and the lower temperature budget paves the way for a large number of potential electronic applications. Temperature and dwell time studies have given some insight into the growth mechanism and will hopefully lead to a more complete growth model for graphene which in turn would help with the optimisation of growth for device implementation.

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