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Synthesis of few-layered graphene by ion implantation of carbon in nickel thin films

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Abstract

The synthesis of few-layered graphene is performed by ion implantation of carbon species in thin nickel films, followed by high temperature annealing and quenching. Although ion implantation enables a precise control of the carbon content and of the uniformity of the in-plane carbon concentration in the Ni films before annealing, we observe thickness non-uniformities in the synthesized graphene layers after high temperature annealing. These non-uniformities are probably induced by the heterogeneous distribution/topography of the graphene nucleation sites on the Ni surface. Taken altogether, our results indicate that the number of graphene layers on top of Ni films is controlled by the nucleation process on the Ni surface rather than by the carbon content in the Ni film.

(Some figures in this article are in colour only in the electronic version)

Graphene is the first stable two-dimensional crystal, discovered in 2004 [1]. Since then, this new nanomaterial has been the object of a large interest due to its peculiar and intriguing properties [2, 3]. Low crystalline quality graphene is already used for several applications, such as composite materials and electrodes for batteries [4]. However, as far as electronic applications are concerned, high quality graphene films are needed as well as robust and reproducible methods to synthesize them.

The first method used to obtain graphene flakes was the mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) [1], which produces high quality crystals with their dimensions in the 10–100 μm range. Although not amenable to large areas and high throughputs, this method has been extensively used to demonstrate the amazing electronic properties of graphene [1–3]. The other early route for the synthesis of graphene films is the epitaxial graphitization of silicon carbide substrates [5]. This technique which has been refined recently [6] now yields graphene domains of ∼50 μm × 3 μm on the terraces of monocrystalline SiC substrates [6]. More recently, the epitaxial growth of graphene films on monocrystalline transition metals such as Ru(0001) has been revisited [7], producing larger graphene domains, with their dimensions in the 200 μm range. A number of recent papers have also shown the interest of polycrystalline graphene growth on non-carbide forming polycrystalline transition metals by decomposition of a carbon bearing gas precursor, in a way similar to chemical vapor deposition (CVD) [8–13]. Here, the idea is to produce graphene domains (∼10 μm × 10 μm or more [14]), larger than the grain size of the supporting metal films or foils and with low defect boundaries. However, this goal seems to be out of reach presently, since the domain size of single layer graphene grown by CVD on monocrystalline (111)-oriented Cu substrates is only of the order of a few 100 nm in both dimensions at best [15] and it is hard to imagine that growth on polycrystalline Cu would yield larger domains.

For those metals in which carbon has relatively high solubilities (e.g., Ni, Co, Ru, …), the metal-assisted CVD mechanism usually involves (i) catalytic decomposition of the
is of carbon ions. The carbon density in one graphene layer on polycrystalline Ni thin films by using ion implantation graphene [13, 14].

limiting, yielding films with essentially one monolayer of growth proceeds through a surface mechanism which is self-limiting, yielding films with essentially one monolayer of graphene onto the metal surface, either at the growth temperature when the solid solution has been saturated, or during cooling, because of the decrease of carbon solubility in the metal. However, for graphene films grown on Ni, it seems difficult to precisely control the number of graphene layers over large areas [14]. When the solubility of carbon in the supporting metal is negligible (e.g., Cu), graphene growth proceeds through a surface mechanism which is self-limiting, yielding films with essentially one monolayer of graphene [13, 14].

In this paper, we explore the possibility to grow graphene on polycrystalline Ni thin films by using ion implantation of carbon ions. The carbon density in one graphene layer is \( \sim 3.8 \times 10^{15} \) atoms cm\(^{-2} \), corresponding to a dose easily accessible to ion implantation. Moreover, ion implantation is a robust technique, developed over the past \( \sim 40 \) years by the microelectronics industry, which could become a method of choice for graphene synthesis. Figure 1 schematically shows the procedure followed in this work. We have used 200 nm thick nickel films deposited by e-beam evaporation on oxidized silicon wafers (SiO\(_2\) thickness \( \sim 300 \) nm). Carbon implantation in those Ni films was performed at an energy of 80 keV (yielding a \( \sim 100 \) nm projected range [16]), using a dose of \( 16 \times 10^{15} \) cm\(^{-2} \) which corresponds to the equivalent of \( \sim 4 \) graphene layers assuming a uniform precipitation of the total implanted C upon cooling and also assuming that C precipitation only occurs at the surface of the Ni film. Actually, let it be said from the beginning, our high resolution transmission electron microscope (HRTEM) observations show that there is no graphene at the Ni–SiO\(_2\) interface nor at the Ni grain boundaries after carbon implantation and high temperature annealing followed by quenching. The implanted substrates were annealed under vacuum (\( \sim 10^{-5} \) mbar) using different starting and stopping temperatures (see below). The annealing was performed by pushing the samples (hosted on a quartz boat) with a stainless steel rod into the furnace which was preheated at the chosen temperature. The stainless steel rod was also used to rapidly remove the samples from the furnace, thus providing efficient quenching conditions.

From the results of Lander et al [17], we have evaluated the C solubility in a 200 nm thick Ni film at different temperatures. We have transformed the data of Lander (\( \ln S = 2.480 - 4.880/T \) where \( S \) is the carbon solubility in weight% C into Ni) into C atoms per cm\(^3\) of Ni, yielding \( S_T = 5.33 \times 10^{22} \exp(4880/T) \) atoms cm\(^{-3}\), where \( S_T \) is the carbon solubility expressed in atoms cm\(^{-3}\) at temperature \( T \). From this formula, with have deduced the C solubility in atoms cm\(^{-2}\) in our 200 nm thick Ni films. Some values of interest for the present study are listed in table 1. In order to avoid complications with the kinetics of carbon out-diffusion from the Ni film due to the decrease of solubility as the temperature decreases [18], the following procedure was adopted after ion implantation: (i) annealing was first performed at 900 °C over 30 min, in order to dissolve all the implanted carbon in the Ni thin film (the carbon solubility in Ni at 900 °C is \( \sim 16 \times 10^{15} \) cm\(^{-2}\)—see table 1) and (ii) the furnace temperature was then slowly decreased to 725 °C (at a rate of 0.5 °C s\(^{-1}\)). During this temperature decrease, the carbon solubility in Ni evolves from \( 16 \times 10^{15} \) cm\(^{-2}\) down to \( 8 \times 10^{15} \) cm\(^{-2}\) (table 1), which means that the equivalent of \( \sim 2 \) graphene layers should out-diffuse and precipitate. Finally, (iii) the samples were rapidly quenched from 725 °C, thus trapping the residual carbon inside the Ni. In this manner, we can control the amount of precipitated carbon at high temperature without knowing the details of the kinetics of carbon out-diffusion from Ni at moderate to low temperature.

Figure 2 shows a typical Raman spectrum taken on a sample processed as explained above (annealing at 900 °C and quenching from 725 °C) and still standing on top of the Ni film. It exhibits the now classical features of graphene, i.e., a small.

**Table 1.** Some C solubility values in a 200 nm thick Ni film.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>725</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>C solubility (×10(^{15}) atoms cm(^{-2}))</td>
<td>8</td>
<td>16</td>
<td>23</td>
</tr>
</tbody>
</table>
Figure 3. SEM image of a Ni film after carbon ion implantation and annealing. The local crystallographic orientation at each pixel has been measured using electron backscattering diffraction (EBSD). The dominant blue color indicates that more than 80% of the Ni grains are oriented within 15° of (111).

Figure 4. Cross sectional HRTEM image showing part of a graphene film with a thickness of four to five layers, extending over the whole top surface of a Ni grain. The inset is a higher magnification picture showing a particular area where four layers can be counted.
high temperature annealing, the implanted carbon diffuses towards dedicated nucleation sites, from where growth takes place, and that some grains are totally depleted of carbon by this diffusion process. This carbon redistribution indicates that the graphene thickness (number of monolayers) is determined by the topography of the nucleation sites (probably steps or bunches of them at the boundary of (111)-oriented Ni grains), rather than by the amount of carbon present in the Ni films, which points toward further study of the graphene nucleation mechanism on Ni thin films. This tendency of graphene to produce a non-uniform film thickness when synthesized on Ni has already been reported [14] but not really explained yet.

Finally, we have used the transfer length method (TLM) [21] to study the electrical properties of our few-layered graphene (FLG) films. For the transfer of FLG films onto Si/SiO₂ substrates, a 1.14 μm thick PMMA layer was first spin coated on top of the samples after annealing. The Ni layer was then etched using a commercial etchant and the PMMA layer was dissolved once the film was deposited on the oxidized Si substrate [8, 9, 12]. The transferred FLG films were then masked and etched in an oxygen plasma and Pd electrodes were evaporated to a thickness of ∼80 nm. A further annealing at 600 °C under vacuum was performed in order to improve contact resistances. Figure 6 shows a scanning electron microscope (SEM) picture of a typical TLM sample on oxidized Si. We have measured sheet resistances varying between 12 and 40 kΩ/□ depending on the location on the host oxidized Si substrate. These high values tend to confirm that the films are not continuous.

In conclusion, we have used the ion implantation of carbon into Ni thin films followed by high temperature annealing and quenching, in order to synthesize FLG. Our first observations indicate that the number of graphene layers in the FLG films is controlled by the graphene nucleation mechanism on Ni rather than by the amount of carbon available in the Ni film. Larger grains from Ni foils (instead of films) or pre-annealed Ni thin films would probably reduce the amount of nucleation centers and increase the overall uniformity of the graphene films.

Acknowledgments

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Note added. While this paper was in the review process, a similar one appeared [22]. The authors also point out the redistribution of carbon after annealing and cooling leading to a ‘heterogeneous graphene thickness distribution on the surface of the Ni film’ and they ‘presume that the graphene growth is driven by the surface properties and morphology of the Ni grain’, which is similar to our conclusions.

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