

Graphene growth on electrodeposited polycrystalline copper and ruthenium

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Graphene grown by CVD on Cu foils has generated interest due to low cost and the prospect of large-area monolayer coverage. The initial nucleation and growth dynamics of graphene play a critical role in determining the final film quality. In this work, we investigate the effects of the electrochemical synthesis onto graphene quality, showing the influence of the Cu-Ru interdiffusion. The growth of good quality graphene layers is also discussed in terms of the role played by grain boundaries and diffusion at the grain boundaries. This comparison shows that the graphene having the best quality is produced using a ruthenium sandwich covering a copper core. This setting avoids contaminations from evaporation and recondensation of copper during thermal cycling due to the CVD process.

Introduction

Graphene is a monolayer of carbon atoms in the sp² hybridization form. It is produced using several methods such chemical or mechanical exfoliation from highly ordered pyrolytic graphite or by chemical vapor deposition on several metals (1). This work is focused on CVD, a production process that can produce thin films exposing the substrate to one or more gaseous precursors in a vacuum chamber at high temperature. Precursors react on the surface of the substrate and produce the desired film. In the case of graphene, the catalytic substrate is usually a metal produced by Electron Beam Evaporation, that is really expensive process if compared to a simple electrodeposition setting. In EBM, an electron beam focused on a target causes atoms to transform into gaseous phase. These atoms then recondensate into solid form, coating the substrate and the entire vacuum chamber with a layer of the anode material. Electrodeposition consists in an electrolytic process in which a current is used to reduce cations of the desired metal which are subsequently deposited at the cathode. Once the samples are produced, the technique used to deposit graphene is the Chemical Vapor Deposition, performed in a quartz tube under vacuum with hydrogen and methane as precursors at 1000 °C. Raman Spectroscopy is used to recognize a well grown graphene layer on each sample after the deposition process. A typical Raman spectrum for a graphene layer must have a peak around 1580 cm⁻¹ in the Raman shift called G peak that is also the typical graphite peak. In the case of graphene, the G peak must be considerably less intense (approximately four times smaller) with respect to another peak, called 2D peak, placed roughly at 2700 cm⁻¹. Another interesting information for the goal of this work can be obtained from Raman

Spectroscopy, because the appearance of a third peak in the spectrum, called D peak and placed around 1350 cm^{-1} , is related to defective graphene pattern. The more intense is the D peak, the more defective will be the deposited graphene (2-4).

Experimental

Four experimental sample settings were used: an electroformed copper layer covered on one side by an electrodeposited ruthenium layer (substrate A), an electroformed copper substrate (substrate B), an electrodeposited ruthenium substrate on silicon dioxide (substrate C) and an electroformed copper substrate covered on both sides by electrodeposited ruthenium (substrate D). Substrate A samples were produced by electroforming a copper foil in an acid copper sulphate electrolyte on polished steel reaching a thickness of about 40 μm , in order to obtain a manageable copper layer. After the deposition the copper foil is detached from the steel plate, the copper surface in contact with the plate is used as substrate for ruthenium deposition in a sulfamic base electrolyte and graphene growth because of the lower roughness. Nevertheless the surface is mechanically polished. The back face of the copper foil is then covered with tape to prevent the formation of ruthenium in the subsequent phase, the electrodeposition of Ru. After electrodeposition, the ruthenium substrate on the copper sample reach an approximate thickness of 500 nm, as shown in figure 1.

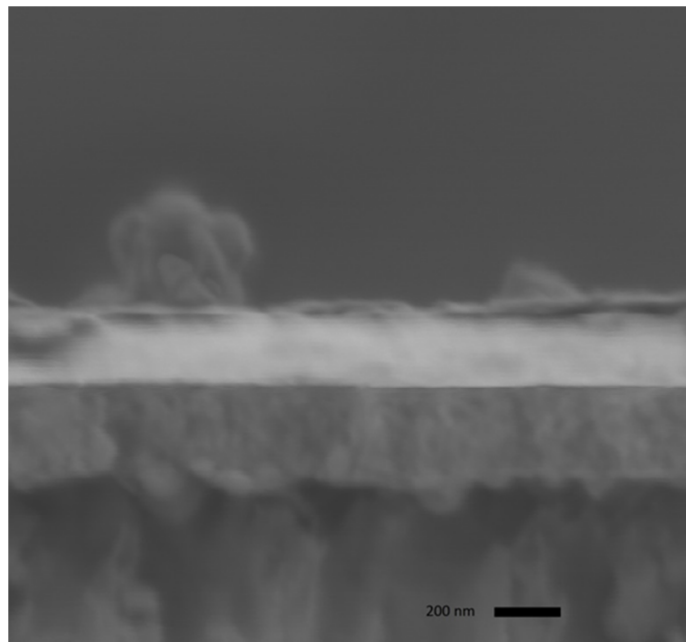


Figure 1. SEM image of the cross section of Substrate A sample; brighter ruthenium layer is shown to detect the thickness.

Substrate B samples are 40 μm thick electroformed copper foils, produced with the same process described above, without the ruthenium electroplating. Substrate C samples are produced starting from substrate A, which are etched with nitric acid to dissolve the copper foil. The remaining ruthenium layer is then transferred onto a silicon wafer with native oxide on top and then dried at room temperature. Substrate D samples are still based on substrate A, but the ruthenium deposition is performed on both side of the

sample. In this case there is no tape on the back side. During ruthenium the polished face is directed towards the platinum anode. This to ensure good current distribution and optimal plating of the substrate, since the back face is not relevant for the deposition of the graphene layer. After production, the substrates are cut (except for substrate C) in approximately 1 cm² slices to be subsequently inserted in the oven chamber that consists in a quartz tube. Before deposition the sliced substrates is cleaned via sonication in acetone and isopropyl alcohol, the sonic cleaning action is maintained five minutes for each step. Before the actual deposition the CVD quartz tube is heated at 800 °C to clean the chamber from impurities, then the furnace is cooled down and when the inner temperature reaches a safe value (usually 200°C) it is possible to load the sample in the chamber. To avoid the oxidation of the sample, the tube is kept under vacuum condition and hydrogen flow since the beginning of the deposition. This solution also helps to clean the sample from native oxidation and keep the surface clean and active for the deposition process (5). Under this conditions (2•10⁻³torr of pressure and 10 standard cubic centimeters per minute of hydrogen) the temperature is set at 1000 °C to anneal and clean the sample. After annealing, 20 sccm of methane are inflated in the tube for 10 minutes (temperature still at 1000°C). This step is the real graphene deposition using methane as carbon precursor. When the temperature in the chamber reaches 600 °C the methane flux is stopped, while the hydrogen is maintained till the temperature of the furnace reaches a safe value to unload the sample. Graphene growth on substrates is then examined with Raman Spectroscopy and a X-ray Photoelectron Spectroscopy.

Results and discussion

The four different substrates were produced to understand the role of diffusing copper through the ruthenium layer in the graphene quality. It is shown the role of copper as promoter of a better quality for the graphene layer on electrodeposited ruthenium foil. All the substrates were treated following the identical graphene deposition process and were subsequently examined by Raman Spectroscopy. Substrate A samples show a typical spectrum with a really small D peak (few defects) and a 2D peak larger than the G peak, confirming a good quality graphene layer. Substrate B samples have a not negligible D peak and a 2D peak comparable with the G peak; this means that the level of quality of substrate B samples graphene is worse with respect to the previous samples. Substrates C show a large D peak but in this case the 2D peak is still larger than the G peak. Despite this last statement, the D peak confirms that the graphene is too defective to be satisfactory. Substrate D samples have a negligible D peak and a 2D peak larger than the G peak. In this case Raman spectrum shows a graphene quality that can be considered superior with respect to the graphene growth on substrate A. Substrate D has a better ratio between 2D and G peaks (closer to the ideal value 4) with respect to substrate A.

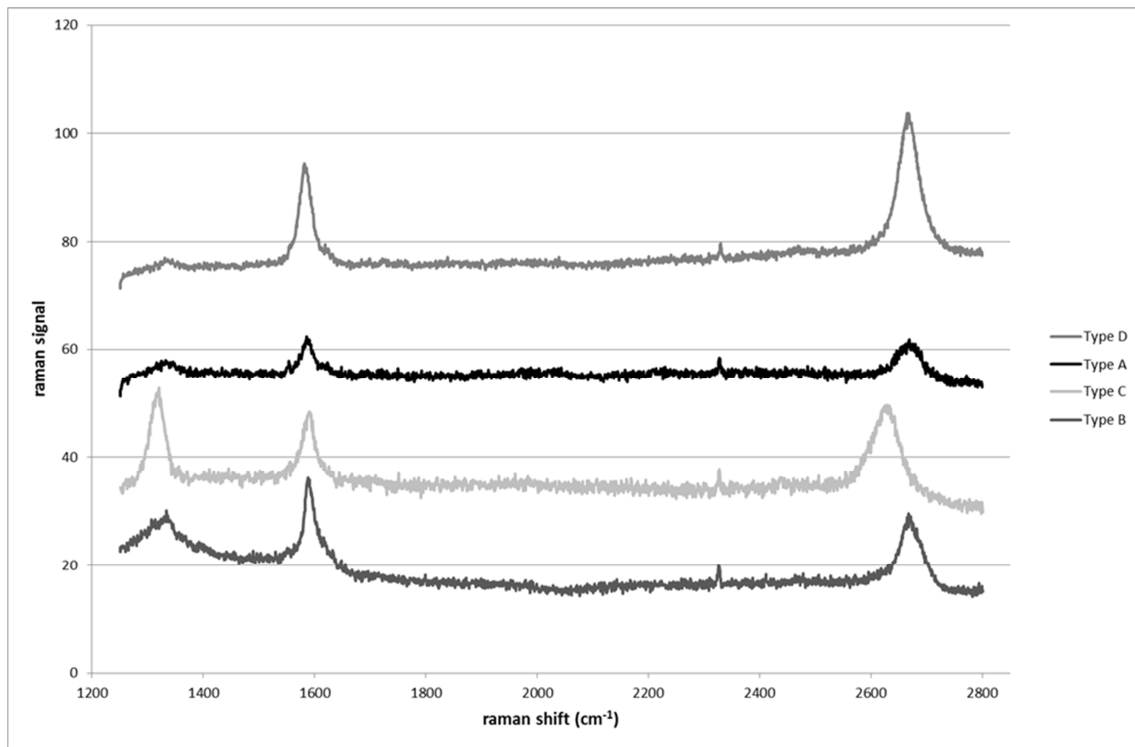


Figure 2. Raman spectra of the four substrate types showing D, G and 2D peaks.

Taking in consideration a comparison among the four Raman spectra reported in figure 2, it can be noticed that the better graphene quality is achieved on top of the samples with both copper and ruthenium. This can result from the annealing of the substrates at high temperature, that promotes a change in the grain size and shape of the ruthenium, while copper can reach the top of the sample. The formation of an alloy between the two elements is hindered (Figure 3) because copper and ruthenium are completely immiscible (6); thus the improvement in the quality of graphene is not related to the formation of a different phase composed by the two materials.

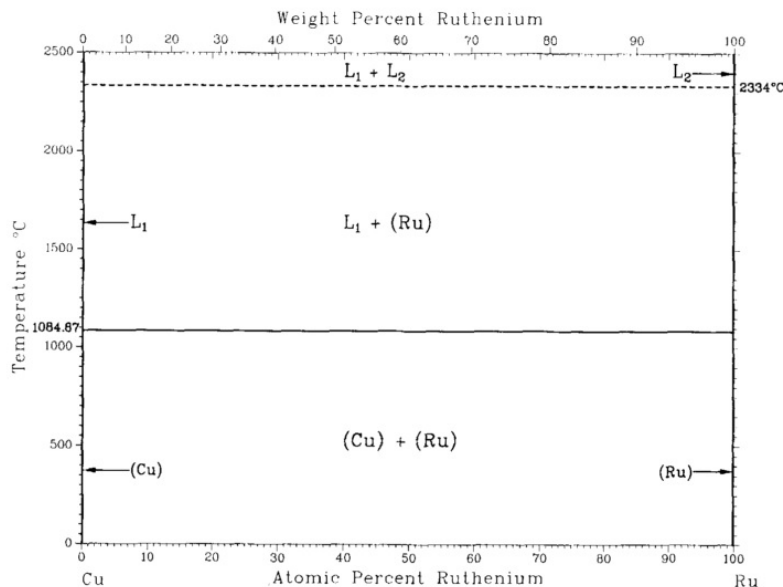


Figure 3. Copper-Ruthenium phase diagram.

Accordingly, the diffusion at high temperature at the ruthenium grain boundary is considered as the main process of migration of copper to the surface. Another possibility to explain the presence of copper on the surface of the substrate is the evaporation of copper from the back side of the sample and the subsequent recondensation on the other side. To stop the evaporation-condensation effect, substrate D sample was thus developed. This type of sample has no copper exposed to the high temperature environment of the CVD chamber. X-ray Photoelectron Spectroscopy was performed to study the amount of copper on top of the samples after the annealing on substrate A, substrate D and on a sample not subjected to previous annealing. XPS detected copper, ruthenium and carbon, the amount of carbon is not reliable and not relevant in terms of the aim of this work, in fact can derive from graphene on the sample or from the environmental carbon. However it is significant to know the ratio between Cu and Ru on the surface of the samples, this proportion depends only from permanence time at high temperature. From XPS curves using atomic sensitivity factors for copper and ruthenium, it was estimated the percentage quantity of copper and ruthenium (and carbon) at the surface. Values are reported in Table 1.

Table 1. Elemental atomic percentage and Ru/Cu ratio for not annealed, substrate A and substrate B samples from XPS analysis.

	<i>Not annealed</i>	<i>Substrate A</i>	<i>Substrate D</i>
<i>% Cu</i>	6.93	22.35	16.48
<i>% Ru</i>	21.93	20.50	36.24
<i>% C</i>	71.14	57.15	47.28
<i>Ru/Cu ratio</i>	3.16	0.92	2.20

The higher Ru-Cu ratio value is reached on the surface of the sample not annealed. Substrate A sample has the higher copper values, this is due to the joint action of evaporation-recondensation and grain boundary diffusion through ruthenium. These phenomena can transport copper to the analyzed surface from the back side and from the core of the sample. Preventing the evaporation-recondensation, an intermediate value of the Ru-Cu ratio in the substrate D sample is observed. The mechanism that can increase the amount of copper on the surface of the substrate must be the grain boundary diffusion. An explanation to the improving quality of graphene on substrate D is that after diffusion, when copper reaches the surface of the sample, its lattice structure is arranged in a better way and can promote a good quality graphene growth acting as nucleation center for the growth of graphene (7). If copper is coming from the back side of the sample via evaporation-recondensation, this behavior cannot be accomplished probably because the condensation of copper is not able to form high ordered nucleation centers on the substrate. Thus graphene on substrate D samples has a better quality despite a minor amount of copper on the surface.

Conclusions

The possibility to grow good quality graphene via CVD process on electrodeposited ruthenium on electroformed copper substrate has been discussed. This work shows that the high quality in the deposited graphene layer is related to the presence of copper on the

surface of the substrate, coming from boundary diffusion through the ruthenium layer. An interpretation based on the presence of highly ordered copper spots on the surface due to diffusion is proposed. Once the graphene deposition process starts, these spots can act as nucleation centers for the growth of the graphene layer.

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