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Graphene Growth on Different Industrial Copper Ribbons by Chemical Vapor Deposition

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Abstract. In our study is investigates the graphene growth on few industrial copper ribbons. The graphene is synthesized by low pressure chemical vapor deposition. Both of the Argon and (Methane/Hydrogen) mixture are the precursors for deposition time. The surface morphology and grain growth behavior of these films are studied by SEM, AFM and OM observation. Impurities on the Cu substrate behave as the nucleation sites in the formation of carbon cluster on Cu surface. The graphene morphologies on these 4 types substrates are constituted by carbon discs in the range of 1~20 μm. Fractal geometry has been observed to study a variety of irregular films within a jigsaw of the variance grain structures. Current results verify the effect of surface impurities on the resulting graphene thin film. We suggest that a higher Cu purity substrate supports formation of larger graphene grain size.

Keywords: Graphene, LPCVD, Industrial Copper

1. Introduction

Graphene growth on Cu substrate through Low Pressure Chemical Vapor Deposition (LP-CVD) is widely reported in literatures. Many important efforts have been conducted to investigate the mechanisms of graphene growth [1-6]. In particular, it has been shown great promise for producing large and predominantly monolayer graphene of excellent quality can be synthesized by CVD on Cu foils. However, the properties of CVD graphene have not reached the requirements of utilization for carrier mobility and uniformity [7-9]. To realize graphene's promise in carbon-based electronics, a full understanding of the mechanisms for film formation and the rational engineering of the growth of wafer-scale graphene are needed. Consequently, the compositions of Cu substrate alloys become a necessary issue for the synthesis of high-quality graphene. Here, we conduct the graphene growth on semiconductor level Cu ribbons which allow low cost. Current study compares the quality of grown graphene formed on different Cu substrates. We systematically analyze the CVD process in the framework of 2D nucleation and growth of thin film which describe the key stages that determine the nucleation density, distribution of nuclei and final coverage. We have found that, both nucleation and growth procedure are affected by the several microscopic substrate features. We focus on the purity of industrial Cu substrate ranging from 87% to 97%. Furthermore, the purities of commonly used Cu foils are usually covered with a layer of oxidation and composed by some other elements, such as Cl, O, C and Fe. We observe the properties of grown graphene around these impurity defects. We find that a higher Cu purity substrate supports formation of larger graphene grain size. Larger-size of grown graphene can be reached by high-temperature CVD process (1050^{o}C) which the nucleation growth can cross the substrate grain boundaries. cu substrate impurities significantly deteriorate the quality of graphene studied by direct observation of optical microscope (OM), Raman spectroscopy and scanning electron microscope (SEM). These results provide deeper understanding of the graphene growth mechanism and have crucial impact for the optimization of graphene quality for various Cu substrates.

2. Experiment

2.1. Pre-treatment of process

To growth the graphene process it can easy divided into three part pre-treatment, growth and transfer. Before the growth process is necessary have pre-treatment process. As the Fig 1 at first cutting the shape of copper as sample. Prepare the HCL to wash the copper the purpose is to remove copper surface oxide. After that use di-water to clean the sample also wash it by ethanol the purpose is to remove excess water. When after clean up the sample use acetone and ethanol to wiping the furnace. Finally it can starting the growth process.

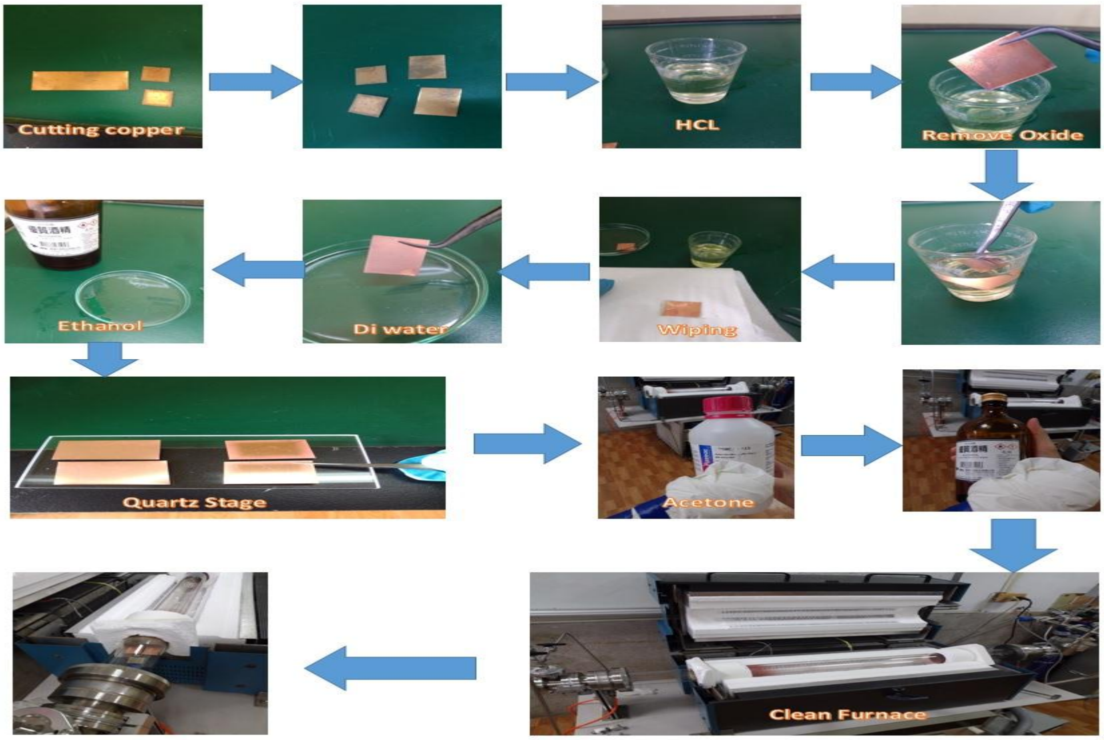


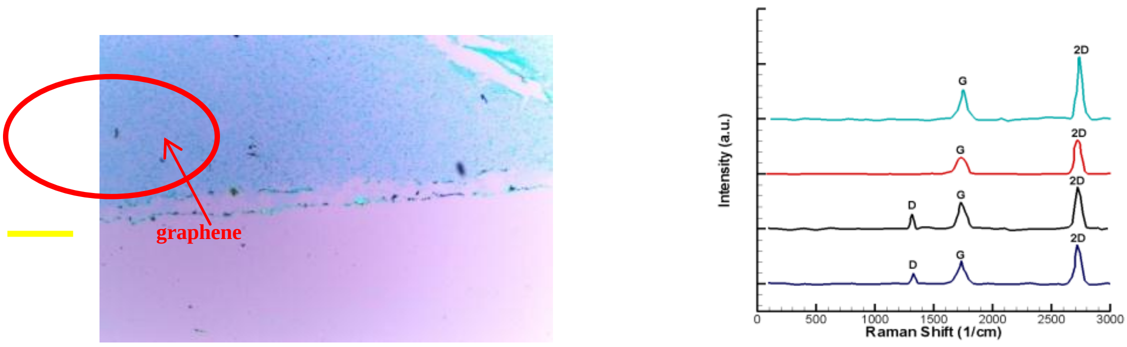
Fig. 1: Schematic process of pre-treatment

2.2. Experimental Parameter

Four types of Cu ribbons (purity:87% ~97%) were commercially obtained from four different companies. First we performed an analysis of the substrates as detected by Energy Dispersive Spectroscopy (EDS). From this detection, we found surface impurities mainly composed of Cu, Cl, O, C, Mg, Si, Al and Fe. The prepared Cu foils were then used to carry out graphene growth. Hydrogen was introduced into the chamber during heating to 1050^{o}C at a rate of 10^{o}C/min ($T_{Cu,melt}$=1085^{o}C). The foils were annealed for 15 min to start Cu grain growth and to clean the substrate surface. Graphene was then performed at 1050 ^{o}C for 60 min under precursor's mixture of CH_4 (60 sccm) and H_2 (120 sccm). After this time, the furnace was turned off and allowed to cool down with both CH_4 and H_2 still flowing. The CH_4 was turned off when the furnace temperature reached to 760^{o}C. We halted growth before the graphene grains merged with each other to form a polycrystalline continuous graphene film. The sample was then rapidly cooled under 15 sccm hydrogen flow. Finally, graphene thin film was transferred by a PMMA assisted process in which Copper was etched by 5% $FeCl_3$, and graphene thin film was transferred onto Si wafer with 300nm SiO_2. And then, the PMMA was dissolved in acetone.

3. Results and discussion

We characterize the graphene grown on four types of substrates by using a Raman microscope, optical microscope (OM) and a Scanning Electron Microscope (SEM). The graphene thin film is prepared by LP-CVD on Cu substrate. Figure 1a shows an optical microscope image of the sample on Si/SiO_2 substrate. As can be seen in Figure 1b, the Raman spectra of graphene on four types of substrates show that they mostly have single-layer (A_{sub} and B_{sub}) to few-layers (C_{sub} and D_{sub}) graphene. To understand the effect of surface impurities of Cu substrate, in first set of experiments, we investigate the influence of substrate's compositions (denoted as A_{sub}, B_{sub}, C_{sub} and D_{sub}). Raman measurements of the graphene film regions that replicate the grain boundary and striated Cu regions indicate that carbon atoms in C_{SUB} and D_{SUB} (Cu~93% and 87%) are mostly in disordered sp^3-bonded networks as evidenced by the high density of the D band (1350 cm^{-1}) and the relatively weak 2D band (2700 cm^{-1}).According to current experiments, the disordered carbon atoms form in grain region when impurities (Mg, Al, Fe, O and Cl) are used as the catalytic substrate. Results represent similar trend with former researchers. The formation of disordered carbon atoms at the surface defects and step edges has been attributed to the fact that carbon atoms are sheltered and attracted to surface irregularities where the atoms diffuse metal edge and nucleate graphene growth. The kinetics of two-dimensional nucleation and growth on surfaces has been observed in current experiment. The results reported here suggest that the mechanism of graphene growth on Cu foil differs from the growth mechanism on pure Cu substrate because of irregularities and impurities. While growth of ordered graphene on Cu foil is less dependent on nucleation at surface irregularities.



(a) (b)

Fig. 2: (a) Optical microscope image shows a CVD-graphene film grown on the Cu-foil after transfer to a Si wafer with 300 nm SiO_2 layer. (b) Raman spectrum of graphene film grown on A_{SUB}, B_{SUB}, C_{SUB} AND D_{SUB} substrate; with colored in cyan, red, black and blue, respectively. scale bar: 1 μm.

Composition elements	**A substrate (A_{sub})**	**B substrate (B_{sub})**	**C substrate (C_{sub})**	**D substrate (D_{sub})**
Cu	**97%**	**95%**	**93%**	**87%**
Cl	**0%**	**0%**	**1.2%**	**1.7%**
O	**0.5%**	**1.3%**	**3%**	**4%**
C	**2.1%**	**1.7%**	**1.6%**	**7%**
Fe	**0%**	**2.1%**	**0%**	**1.5%**
Al	**0%**	**0.3%**	**0.7%**	**0.7%**
Mg	**0%**	**0%**	**0%**	**1.4%**
Si	**0.2%**	**0.6%**	**1.5%**	**1.8%**

Table 1. the compositions of 4 Cu substrates

The characteristic diameters of the growth carbon islands are about 5~20μm. On the other types of substrate, for graphene growth on C_{SUB} and D_{SUB} (lower Cu purities substrate), the carbon islands are about 0.1~1μm which are 1~10 order smaller than higher Cu purities substrates. It is informative to say, in current experimental condition (T=1050^{o}C), the impurities induced nuclei rapidly connect the radical carbon atoms (sp^3 orbit) to form local carbon discs. Interestingly, the SEM images show that the characteristic fractal-like patterns of graphene growth on lower purity (C_{SUB} and D_{SUB}) substrates. The graphene grains are typically with 120^{o}C corners on highest purity substrate (A_{SUB}). This suggests that the graphene edges are parallel to specific crystallographic direction. For B_{SUB}, C_{SUB} and D_{SUB}, the nucleation shapes are notably different from the hexagonal-like shape, but are similar to fractal-like patterns. Recent experimental and theoretical studies of graphene on single-crystal Cu (111) had also found that individual graphene grains can be grown continuously across Cu grain boundaries or surface defects, as shown in Figure 3. This reflects that the weak influence of the Cu crystal lattice on graphene growth. But for C_{SUB} and $D_{SUB,}$ surface impurities induced nuclei formation results in a disordered carbon structure and closely connects with smaller carbon discs which might be resulted in polycrystalline graphene with smaller grain sizes. The carbon preferentially migrates away from the impurities which constrain graphene growth.

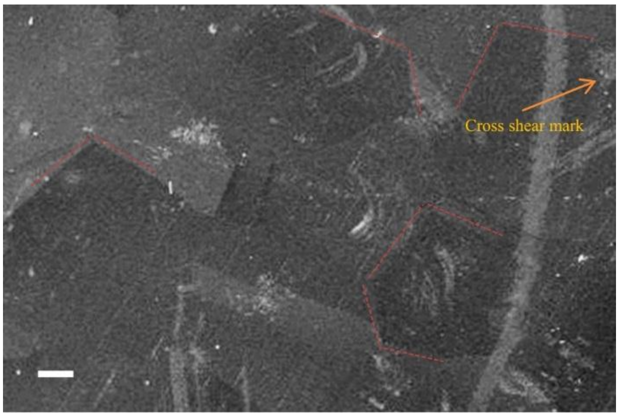


Fig. 3: Scanning Electron Microscope (SEM) images taken at 7kV; graphene growth on A substrate (A_{sub}); SEM images showing that carbon islands, with ~120^{o}C corners and graphene grains can be continuously cross shear mark and defects. The CVD growth time:60 mins; Scale bar: 5 µm.

Extensive EDS analysis is performed in figure EDS spectra from the nucleation centers show that most of them are composed by Fe, Al, Si and Mg or their corresponding oxides. Substrate composed only by Cu on the same sample is also present, as shown in Figure 4, where an EDS pattern from the islands confirm they are only composed by carbon and Cu (Fig. 4).

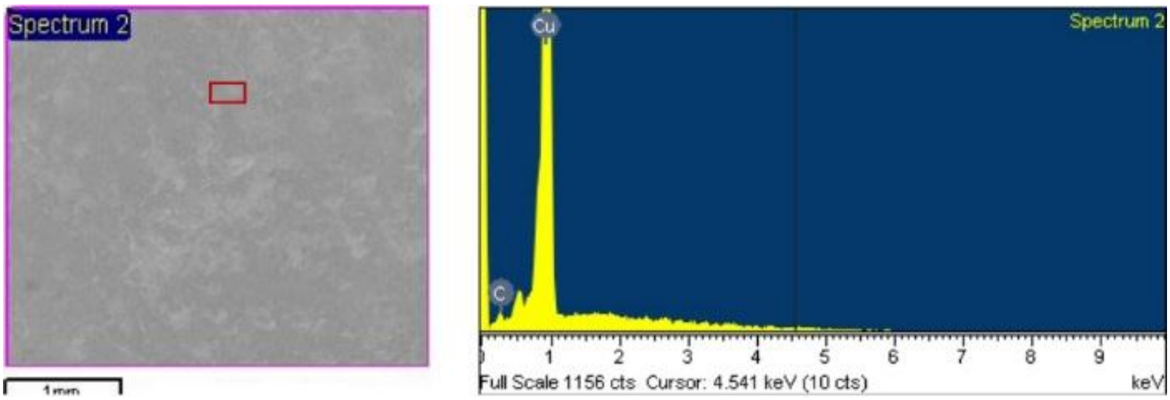


Fig. 4: EDS characterization of a carbon islands on the Cu surface. (a) SEM image of carbon islands and (b) Energy Dispersive Spectroscopy (EDS) spectrum captured from the selected region shown in (a).

Recall the Raman measurements, the patterns confirm the formation of graphene on the Cu substrate. Graphene at 1050^{o}C seems to occur by diffusion of the carbon atoms on the cooper surface. We observe larger carbon accumulations around the surface impurities (where the D band Raman spectra were observed). In current study, our annealing temperature is 1050^{o}C (~1320K); therefore graphene growth in current experiment is closer to the higher temperature regime where the surface impurities will be present clearly. Results reveal that the step-edge nucleation can also be commonly occurred on higher impurities surface even at higher annealing temperature. Raman spectroscopy is employed to further confirm this point. Alternative copper substrates for graphene growth include certain level impurities in a range from 3% to 13%. CVD process on such industrial substrate is not conducted by previous studied. Surprisingly, however, we observe an effective result for graphene growth. In case of samples with higher surface impurities, more step edges occurred. The presence of disordered structures may be resulted in less carrier mobility and reduce the performance of graphene.

4. Conclusions

We grow a graphene thin film on different types of industrial copper ribbons through LP-CVD. Large areas of the graphene are analyzed with SEM-EDS. According to the results, we verify the effect of surface impurities on the resulting carbon thin film. The formation of such carbon nanostructures instead of graphene growth and are the subject relevant in industrial graphene fabrication based on these copper ribbons. In summary, we demonstrate the industrial-level Cu substrates for CVD growth of graphene. The coverage of graphitic thin film grown on lower purity substrate is nearly 1.3 times more than high purity one by the same process. But the quality of the graphene thin film on high purity substrate is better than low purity one. These findings provide better insight in to challenges for industrial graphene fabrication but also suggest the limitation of surface contaminants in the graphene formation process.

5. Acknowledgement

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