Redistribution of Carbon Atoms in Pt Substrate for High Quality Monolayer Graphene Synthesis

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Abstract

Due to its fascinating electrical and mechanical properties, graphene has attracted increasing attention since being mechanically exfoliated from bulk graphite[1]. Many graphene production techniques have been developed. Among these, CVD growth using metals as substrates is the foremost way to synthesize large area graphene with relatively acceptable uniformity. However, there are always many flakes of multilayer or few-layer graphene (2~4 layers) [2] using this method. The random existence of the multilayer flakes strongly influences the performance of graphene FETs and circuits. This paper discusses the CVD growth mechanism of monolayer graphene on Pt substrate and presents an improved process to reduce the density and size of multilayer and few-layer graphene flakes.

Platinum films are used as substrate in this work and the basic mechanism of graphene growth on Pt substrate is based on carbon segregation or precipitation[3]. Curve (Ⅰ) in Figure 1(a) shows the temperature profile of the traditional graphene synthetic process. Normally, the process consists of four stages: 1) temperature rising in H_2 ambient, 2) annealing stage in H2 ambient 3) decomposition stage. 4) cooling or graphene forming stage. Because of the non-uniform distribution of the dissolved carbon atoms and the short cooling stage, graphene grown on Pt surface in the cooling stage tends to maintain the distribution characteristics of the dissolved carbon atoms in Pt foils in the decomposition stage. In this paper, we introduce a redistribution stage before cooling to allow the carbon atoms to diffuse in Pt substrate. Then, a graphene film with less multilayer graphene flakes is promising to obtain. An improved experimental process as shown in Figure 1b (Ⅱ) was designed and carried out and the detailed parameters are shown in Table 1.

Figure 2 shows the SEM images of the graphene grown in different process conditions. In order to quantify the experimental results, four parameters are introduced for result discussion (To simplify the calculation, we call both multilayer and few-layer graphene flakes multilayer graphene hereinafter): 1) N_{multi} , the amount of multilayer flakes in a given area (600 μm*600 μm in this paper when the SEM image is with 500X magnification), 2) $A_{ave\ multi}$, the average area of multilayer graphene flakes, 3) R_{cov}, the coverage ratio of graphene on the surface of Pt substrate, 4) $A_{ave\ mono}$, the average area of monolayer graphene, this parameter is obtained from the formula (1),

$$A_{ave\ mono} = \frac{A_{total} - A_{ave\ multi} * N_{multi}}{N_{region}} \quad (1)$$

where N_{mul}, $A_{ave\ multi}$ and $A_{ave\ mono}$ are defined as above, A_{total} is the given area (600 μm*600 μm in this paper) and N_{region} is the maximum amount of triangle regions on the area divided by multilayer flakes. It can be derived from Euler's formula (2)

$$N_{region} = e - v + 2 \quad (2)$$

where v is s N_{multi}), and e=3(v-2) is the maximum amount of line segments mutually disjoint to each other connected from the vertices v. This parameter $A_{ave\ mono}$ implies the average intact area that can be used for device or circuit fabrication without any multilayer flakes. The relationship between the four parameters and redistribution duration is shown in Figure 3.

Raman spectroscopy was used to evaluate its quality. 18 random points on the monolayer graphene were sampled to take Raman spectra. The narrow distribution ranges of FWHM of 2D and G band prove the high uniformity and high quality of the graphene grown on Pt substrates by the improved method.

Based on the experimental results which are shown in Figure 2 and 3, the introduced redistribution stage strongly affects the quantity and size of few-layer and multilayer graphene flakes on the CVD synthesized graphene. For the graphene sample grown with 60-minute redistribution duration, parameter $A_{ave\ mono}$ is about eight times larger than that of graphene grown without the redistribution stage. But when the redistribution stage is very long, eg 60 minutes, the coverage of graphene on the Pt substrate is no longer 100%.So the optimal duration of the redistribution stage should be between 40 and 60 minutes for our study.

References

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Figures

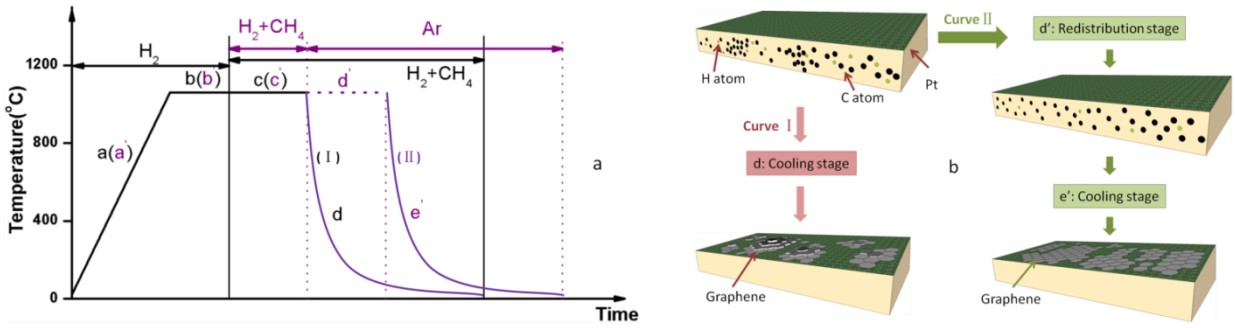

Figure 1. (a) curve (Ⅰ) and (Ⅱ) are the temperature profiles for graphene synthesis on polycrystalline Pt foils without and with a redistribution stage.(b) the schematic diagram of the two different graphene growth processes.

Table 1 graphene growth parameters

Exp.	Process temp (℃)	H_2 flow rate (sccm)	CH_4 flow rate (sccm)	Decomposition time (minutes)	Ar flow rate (sccm)	Redistribution time (minutes)	Cooling rate
S1	1060	794	6	8	20	2	about 200℃ /min at the first three minutes
S2						20	
S3						40	
S4						60	
S0	1060	794	6	40	0	0	

S0 is the process without a redistribution stage for comparison. Considering the intense etching reaction of H_2 to graphene in the cooling stage, a longer decomposition stage (40 minutes here) is essential to get a full coverage of graphene by the method without a redistribution stage.

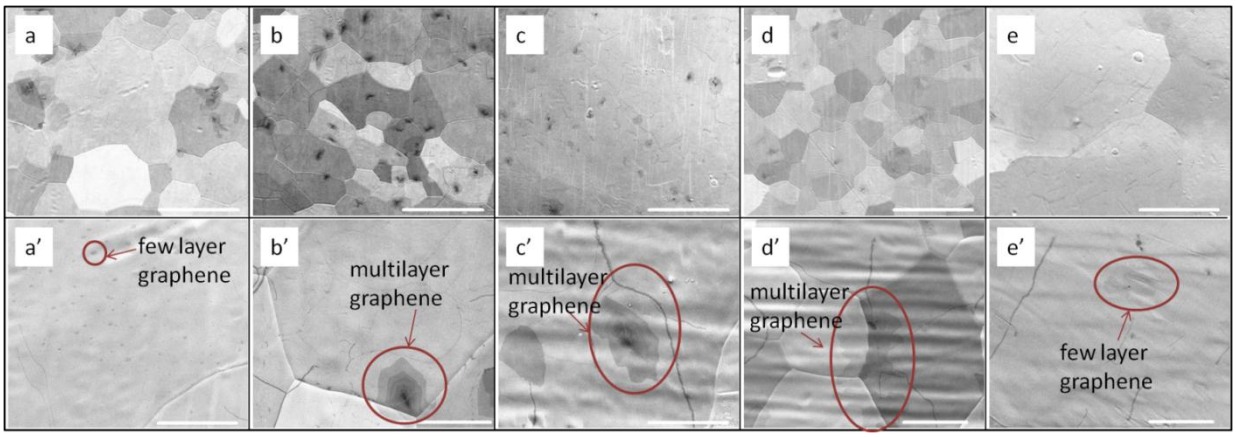

Figure 2. SEM images of graphene grown on polycrystalline platinum foils. a) graphene synthesized without the redistribution stage. Graphene synthesized by the improved method with b) 2 minutes c) 20 minutes d) 40 minutes e) 60 minutes of the carbon atom redistribution stage. a') – e') are images with larger magnification corresponding to a) – e), respectively. The scale bars in a-e are 200 um, and 50 um in a'-e'.

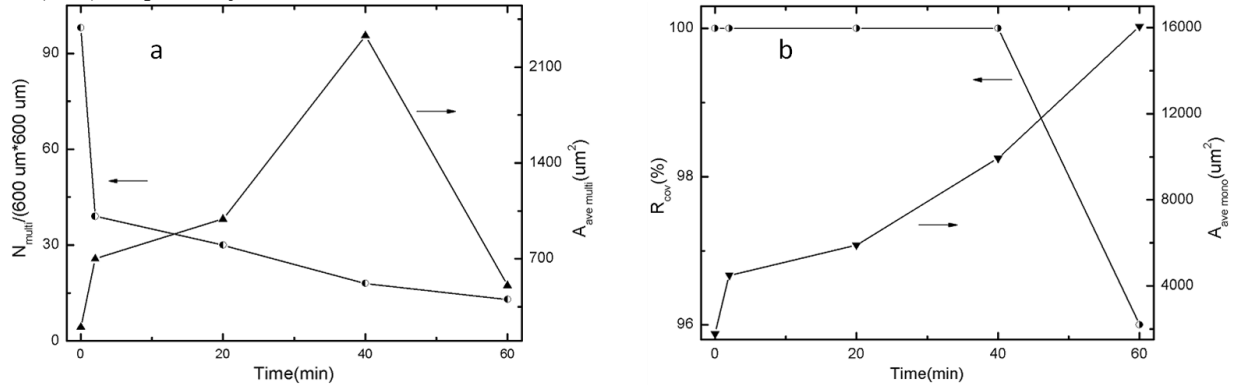

Figure 3 a) the relationship between parameter N_{multi} and $A_{ave\ multi}$ and the duration of the redistribution stage. b) the relationship between parameter R_{cov} and $A_{ave\ mono}$ and the duration of the redistribution stage.