Large-scale single layer graphene synthesized by optimized APCVD method

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Abstract

It is observed that the cooling conditions, including the cooling rate and cooling atmosphere, are the key parameters to control the coverage, thickness, and uniformity of graphene growth on Platinum by atmospheric pressure chemical vapor deposition (APCVD) method. As show in Table 1, a series of experiments were carried out with different cooling parameters to examine the cooling condition effects in detail for the first time. The objective of this study is to find out the optimized growth conditions for large-scale, single layer graphene growth. The surface morphology which reveals the coverage and uniformity of the grown graphene was observed by SEM directly on Pt substrate, and observed by optical microscope (OM) after transferring the graphene to SiO_2(300nm)/Si substrates. As shown in Fig. 1, the fast cooling group gave the coverage of graphene almost 100% under different gas compositions. The deep colored sheets in the OM images indicate multi-layer graphene islands. As shown in Fig. 1b, c, e and f, the size of multi-layer graphene islands is reduced when H_2 was introduced in the S2 and S3 samples. The smallest size and least amount of multi-layer graphene islands are observed in the mixture gas (CH_4 and H_2) environment. For slow cooling group, as shown in Fig. 2, the graphene coverage is much less and large separation of grown graphene sheets could be found. Only small pieces of graphene, as shown in Fig. 2b and e, could be observed in the case of H_2 environment. Based on those experimental results, in general, the graphene coverage is higher with fast cooling conditions than slow cooling ones. Fast cooling with the mixture gas of H_2 and CH_4 environment offers preferred single-layer graphene growth.

Four-step reactions are proposed to explain the graphene growth mechanism during cooling process: 1) release: carbon atoms segregate from Pt and bond to each other to form graphene structures[1], 2) etch: the bonded carbon atoms could react with H_2 during cooling down to form C-H bond, and graphene is etched[2,3]; and 3) thermal decomposition: carbon atoms (from CH_4 thermal decomposition) participate in forming graphene on Pt surface; and 4) diffuse: instead of release from Pt, the dissolved carbon atoms diffuse in the substrate[4]. As shown in Fig. 3, depending on the cooling conditions, only partial of those four-step reactions happened in the designed experiments from S1 to S6. In the fast cooling group, the diffusion reaction doesn't occur because the carbon atoms couldn't get enough time to diffuse into Pt before the system cools down to low temperature. The cooling atmosphere affects the reaction process significantly. In S1 experiments, only Argon gas is used during cooling down. The etching and thermal decomposition reactions don't occur because of the absence of CH_4 and H_2. Only carbon atoms release step was happened. Single-layer graphene films are formed in the low carbon concentration region and multi-layer graphene islands are found in the high carbon atoms concentration region (as shown in Fig. 3). In S2 experiments, only hydrogen gas is used during cooling down. Both carbon atoms release and etch reaction steps occurred. Some weak-bonded carbon atoms structure could be more easily etched away by H_2. Due to the etching effects, the graphene coverage is lower and the size of multi-layer graphene is smaller in comparison to Ar atmosphere case. In S3 experiments, both CH_4 and H_2 gases were used during cooling down. Three reactions occurred and the resulted graphene films are combined effects from carbon atoms release, etch and CH_4 thermal decomposition. Since CH_4 could provide additional carbon atoms and H_2 could etch away weak bonded carbon atom structures, the graphene coverage is the highest with single layer graphene, as shown in Fig. 3. While in the slow cooling cases, carbon atoms could get enough time to diffuse in Pt and react with H_2 before the temperature falls. This effect will reduce the carbon atoms participating in forming graphene, resulting in lower graphene coverage and uniformity on Pt surface. Particularly, for S5 experiment, the H_2 etch effect is enhanced by the slow cooling rate, the etching process become dominant during cooling step and removes almost all graphene.

Fast cooling in mixture gas of CH_4 and H_2 is the optimized choice for growing good quality and single-layer graphene with high coverage. As shown in Fig. 4 to Fig. 7, various characterization techniques (Raman, OM, SEM, TEM, AFM, etc.) were applied to examine the graphene morphology and quality. Back-gated field effect transistor was fabricated (OM image of the device is shown in Fig. 8) and the extracted carrier mobility is up to 1,600 $cm^2V^{-1}s^{-1}$.

Table 1. Cooling conditions for experiments S1 to S6

Index	Cooling Rate	Cooling Atmosphere
S1	Fast	800sccm Ar
S2	Fast	800sccm H_2
S3	Fast	800sccm Mixture of CH_4 and H_2 (CH_4:H_2=0.076:1)
S4	Slow	800sccm Ar
S5	Slow	800sccm H_2
S6	Slow	800sccm Mixture of CH_4 and H_2 (CH_4:H_2=0.076:1)

References

1. M. Gao, Y. et.al, *Appl. Phys. Lett*. 2011, 98, 033101
2. I. Vlassiouk, et.al, *ACS Nano*, 2011, 5, 6069.
3. M. Losurdo, et.al, *Phys. Chem. Chem. Phys.* 2011, 13, 20836.
4. Q. Yu, et.al, *Appl. Phys. Lett.* 2008, 93, 113103.

Figures

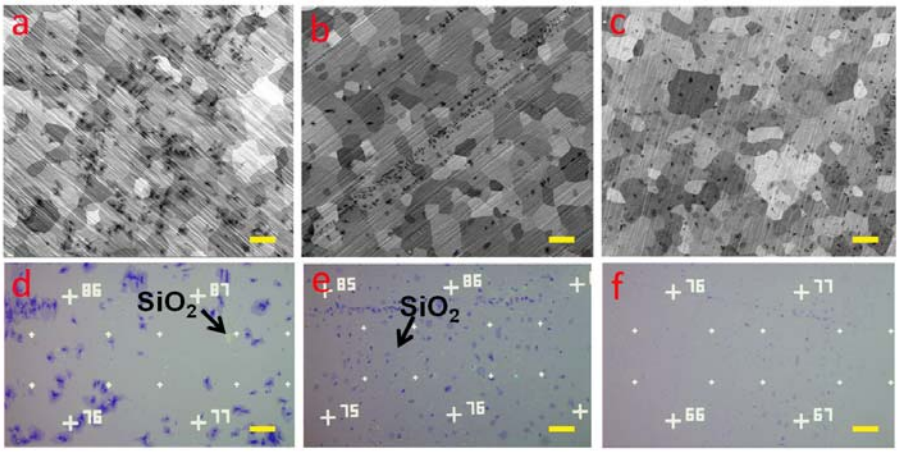

Fig.1. SEM and OM images of the transferred graphene films grown on Pt substrates with fast cooling. (a), (d). 800sccm Ar, (b), (e).800sccm H2, and (c), (f). 800sccm mixture of CH4 and H2(0.076% CH4). Scale bars are 100μm.

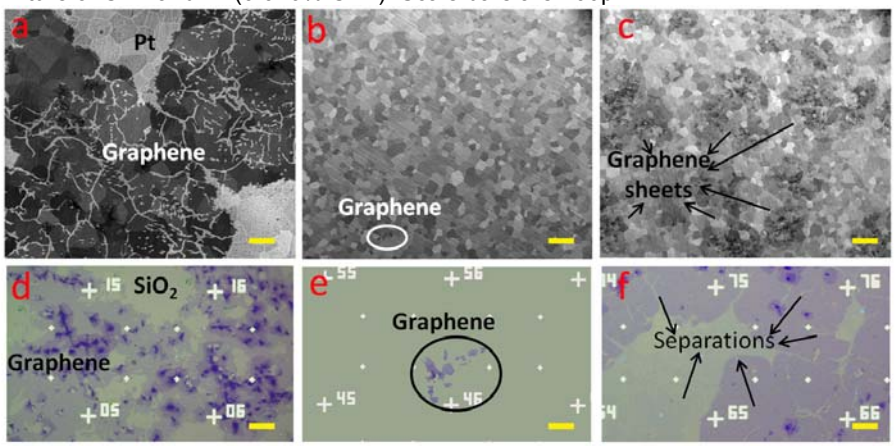

Fig.2. SEM and OM images of the transferred graphene films grown on Pt substrates with slow cooling. (a), (d). 800sccm Ar, (b), (e). 800sccm H2, and (c), (f). 800sccm mixture of CH4 and H2 (0.076% CH4). Scale bars are100μm.

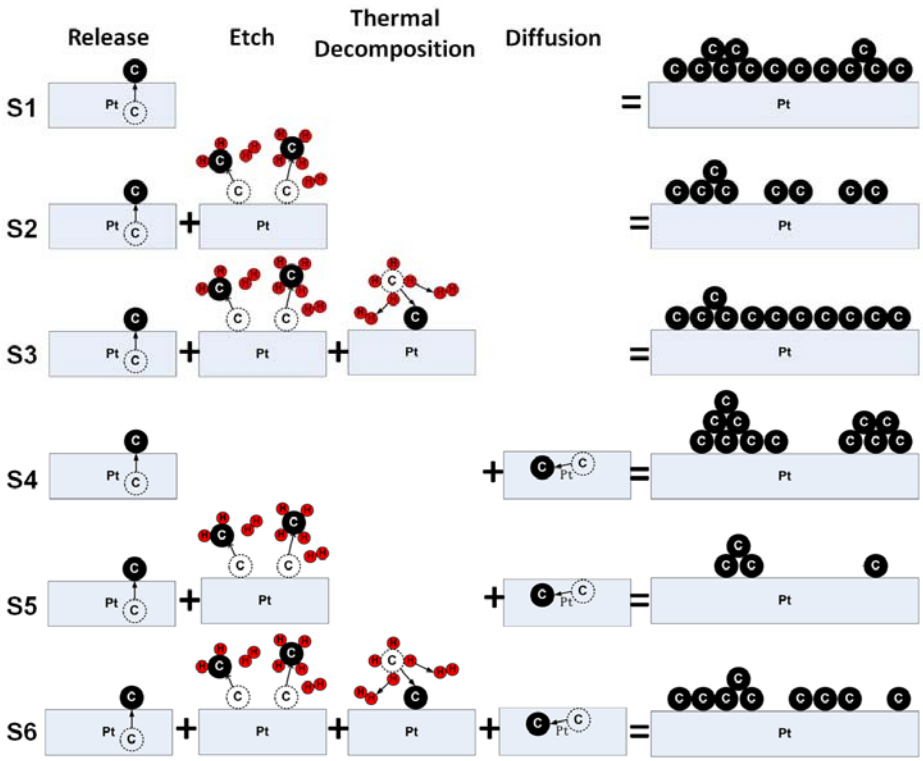

Fig.3. The reactions during cooling effect and the resulted carbon atoms distribution on Pt substrate after cooling in experiments S1 to S6.

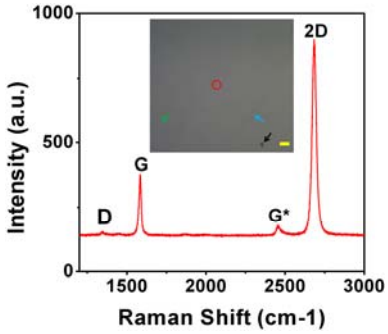

Fig.4.(a) Raman spectra of single-layer graphene. Inset shows the optical image of single-layer graphene. The multi-layer island, wrinkle and residue PMMA caused by transfer are indicated by the black, blue and green arrows, respectively. The Raman sampling point is marked out by red circle. Scale bar is 100μm.

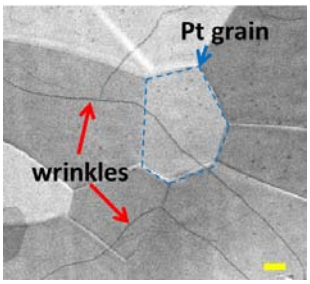

Fig.5. SEM image graphene grown on Pt. Scale bar is 10μm.

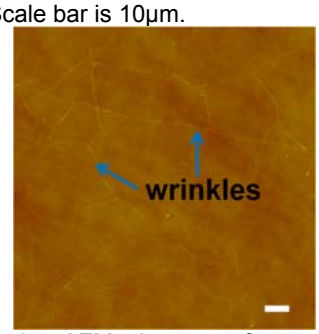

Fig. 6. AFM image of graphene transferred onto Si substrate with 300μm SiO2. Scale bar is 1μm.

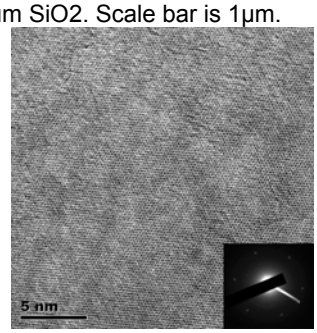

Fig.7. HRTEM image show excellent crystallinity of graphene film. Inset shows the electron diffraction pattern of the graphene film.

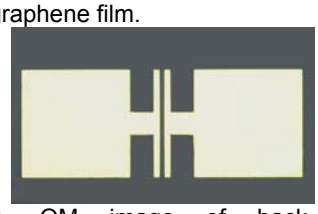

Fig.8. OM image of back-gated graphene FET.