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# STUDYING THE MECHANISM OF GRAPHENE FORMATION BY CHEMICAL VAPOR DEPOSITION SYNTHESIS

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*Due to their unique properties, 2D materials have a great potential in various applications. It argued that chemical vapor deposition (CVD) method is widely used in the synthesis of graphene. In this paper the experiments results of the synthesis of graphene layers by Chemical Vapor Deposition (CVD) method on the copper (Cu) foil discussed. However, desired quality of graphene layers is not always achievable. Therefore, controllable synthesis in domain size and morphology is required for large-scale applications. Examples of the synthesis parameters of polycrystalline and monocrystalline graphene are given. Mechanism of graphene formation studied during the synthesis process. The sample preparation processes and the main growth mechanisms of multilayer and single-layer graphene by the CVD method discussed. Obtained CVD graphene layers characterized by Raman, AFM and SEM analysis.*

***Keywords***: *two-dimensional materials, synthesis, CVD, graphene;*

## Introduction

Graphene is the first representatives of two-dimensional materials. It is quite interesting material with the thickness of one layer of carbon and has a hexagonal modification. Due to their unique properties, graphene has a potential in the various applications for science and technologies, particular in electronics.

There are a few methods of two-dimensional materials synthesis such as mechanical exfoliation, chemical methods. The mechanical exfoliation is top-down type means splitting of large structures like graphite. The first graphene layers obtained with this method by Gale and Novoselov. The second method is the types of chemical vapor deposition, where the formation of structures comes from the gaseous phase during the decomposition of hydrocarbons.

The CVD synthesis recognized as a reliable method of obtaining high-quality two-dimensional (2D) materials [1]. The production of mono and polycrystalline graphene by the CVD method is two different process, but similar as well. However, there are several key factors, which are distinguishing the single-crystal graphene growth on CVD. One of the main parts for single-crystal graphene growth is preventing the premature crystallization. In addition, the substrates treatment such as elimination of impurities, oxides, defects and other structures contribute to the nucleation and graphene growth. The effect of precursor concentration is also an important factor in the growth of single crystals graphene. One of the main advantages is controlling the synthesis parameters, which allows the synthesis of graphene desired size. Where the synthesis parameters include chamber pressure, temperature heating and cooling, synthesis time, and gas composition and flow rate.

The process shown here is suitable to obtain single-crystal graphene with wafer size. In order to achieve this, deep understanding of graphene growth mechanism and requirements for graphene grain growth needed. According to data, the Cu based graphene growth mechanism (Figure 1a) and reaction conditions are shown where graphene nucleation density is reduced and possibility of growing larger graphene domains by using an extended growth conditions (Figure 1b) [1].

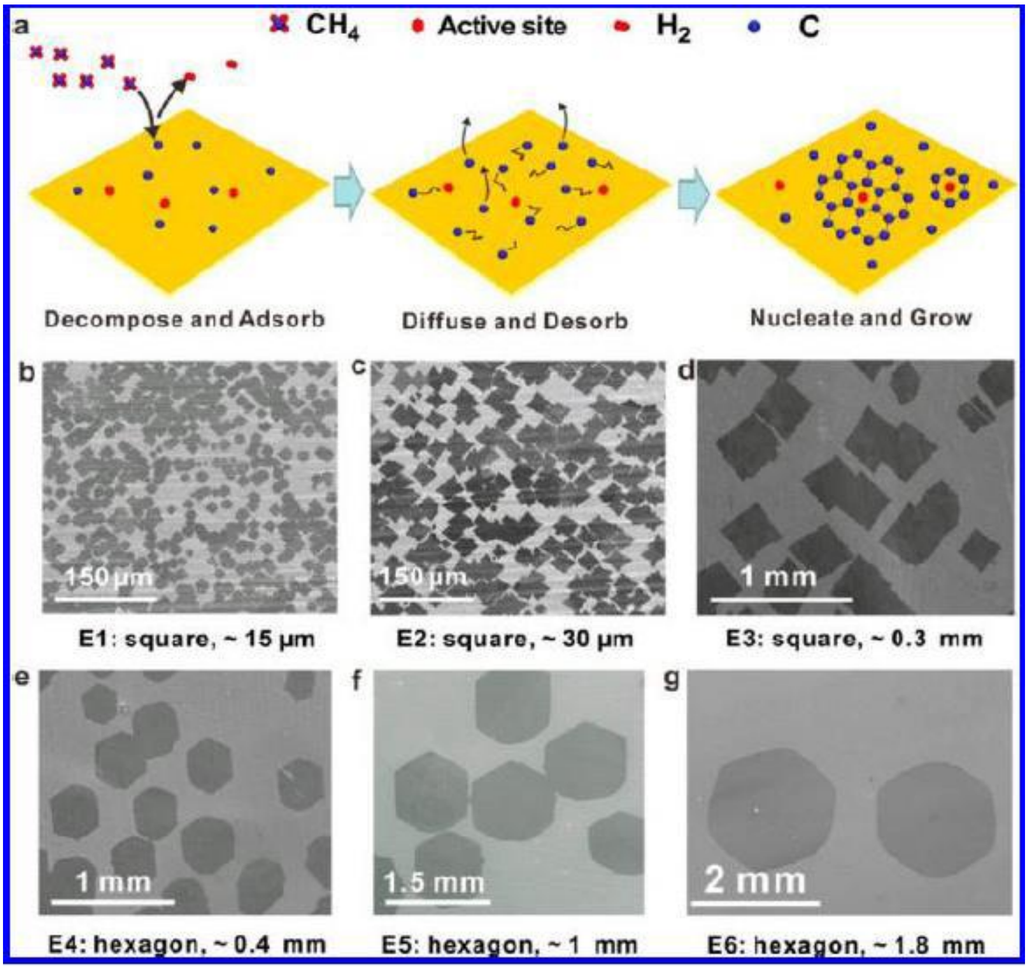

**Fig.1**. Illustration of the Cu-based graphene growth mechanism and the influence of different parameters on the graphene domain sizes and shapes. (a) Scheme for the Cu-based graphene growth mechanism. Here, red hexagons are used to symbolize the active sites of the Cu surface, and blue spots signify active carbon species $(CH_{x<4})_{s.}$ From the proposed mechanism, the active carbon species from the dissociated $CH_4$ are apt to agglomerate into thermodynamically stable $(C_nH_y)_s$ species on the active sites of the Cu surface to initialize the graphene growth. (b-g) Typically SEM images of graphene synthesized under different growth conditions: b (E1), c (E2), d (E4), f (E5), and g (E6) [1]

Many studies point to the importance of oxygen in the process of single-crystal graphene growth by the CVD method. Gan et al. showed that soft oxidation of copper substrate before annealing leads to obtain suitable size of copper nanoparticles (Fig. 2a, b) [3]. Copper nanoparticles contributed to nucleation and growth of large single crystals of graphene. In this work, the onset of oxidation identified as the microscopic amount of oxygen in the Ar gas stream or residual oxygen in the CVD chamber. Hao et al. conducted a detailed study of the effect of oxygen at CVD synthesis of graphene process (Fig. 2c) [4]. Different concentrations of oxygen on copper substrate studied by using copper foils with different purity classes, changing the pressure during cleaning process and supplying pure oxygen before graphene growth. Studies have shown that oxygen on the surface of copper substrates reduces the concentration of active centers by surface etching. Thus suppresses early nucleation and promotes the growth of a single-crystal graphene structure.

Magnuson et al. proposed a new view on the role of oxygen in the process of oxidation of copper substrates [5]. Intentionally oxidizing copper substrates formed a layer of copper oxide, which decompose during subsequent annealing and synthesis processes, thereby eliminating residual carbon from the substrate. This behavior called "self-cleaning". There are also other excellent studies of the observation of graphene growth [6].

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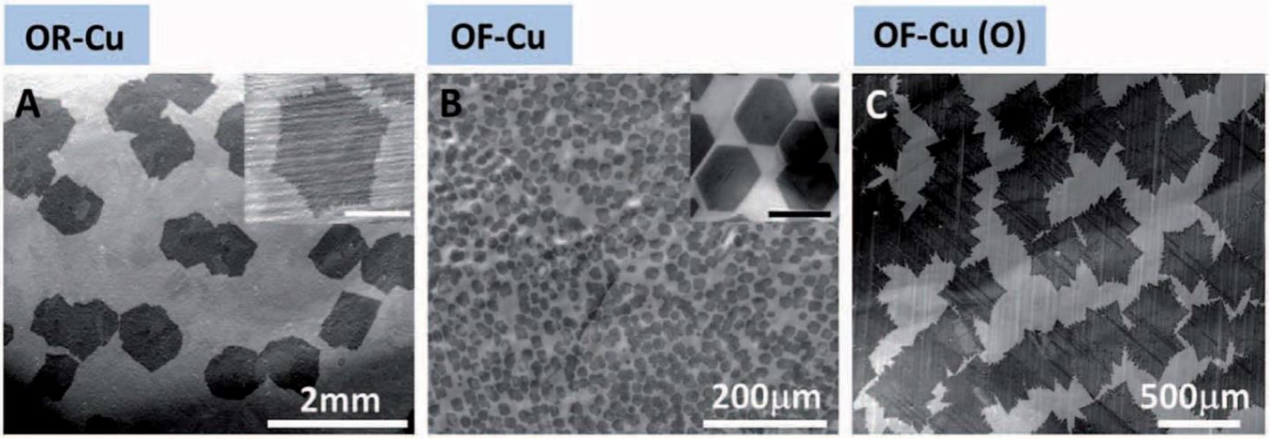


**Fig.2.** The effect of oxygen on nucleation density and shape of domains on different types of copper substrates: OR-Cu (a) low purity copper substrate; OF-Cu (b) high-quality copper substrate; OF-Cu (O) (c) high-purity copper substrates when exposed to oxygen before the start of graphene deposition [5]

However, a deeper understanding of the influence of oxygen desired in order to understand the full role and mechanism of oxygen atoms while achieving excellent control over the process.

## 1. Experimental part

CVD setup assembled at the Institute of Physics and Technology (Fig. 3), which includes three zones tube furnace with quartz reactor, and installed gas inlet system. In this system, triple gas supply used: argon, hydrogen and methane.

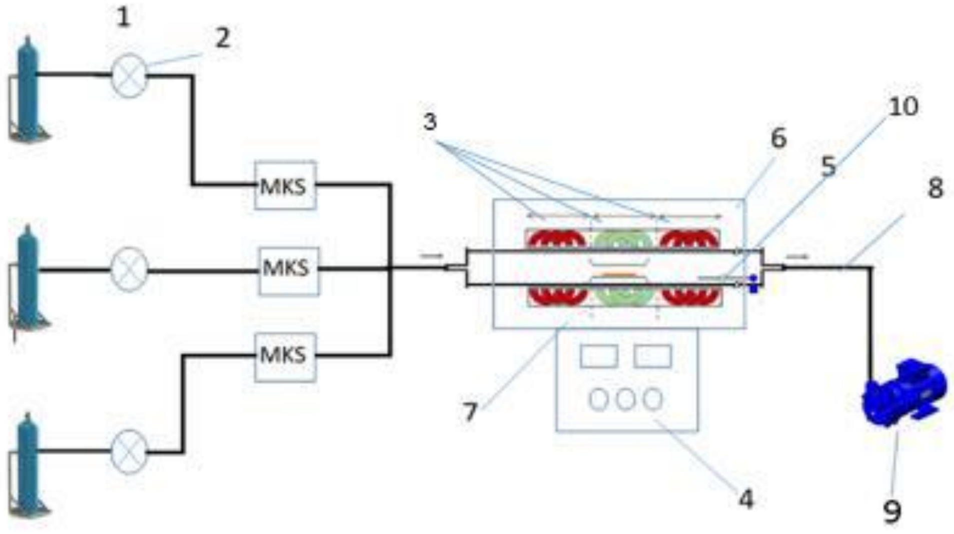


**Fig.3.** CVD setup for graphene synthesis: 1 - cylinders with gases (Ar, $CH_4$, $H_2$); 2 - gearboxes; 3- gas supply controllers; 4 - thermal controller; 5 - quartz tubular reactor; 6 - heating elements; 7- metal substrate; 8- pumping line; 9- mechanical pump; 10-holder; 11-magnet.

Methane plays the role of carbon source for graphene formation. Optimal parameters selected, synthesis of graphene carried at 1050 °C, and the ratio of gases: $CH_4$: $H_2$: Ar is 0.25: 0.5: 3. The synthesis time is 20 minutes.

## 2. Results and discussion

Graphene synthesized on copper substrate, due to its catalytic properties, copper is one of the main materials used in graphene synthesis. In studying the graphene formation on copper substrate was determined that the initial stage is carbon atoms adsorption on the surface. Then, graphene islands formation with same orientation. Subsequently, association of separate graphene islands without defects on the boundaries and high-grade monocrystalline graphene layer (Fig.4).

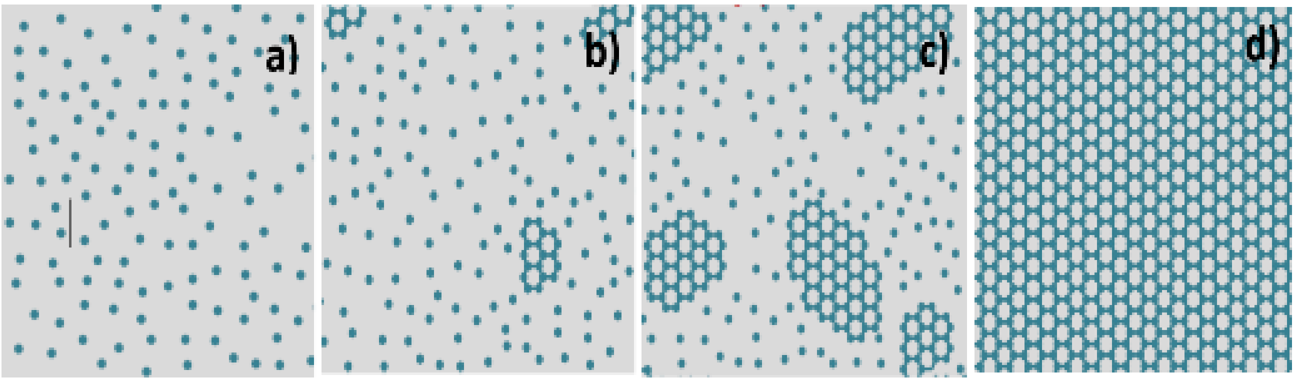
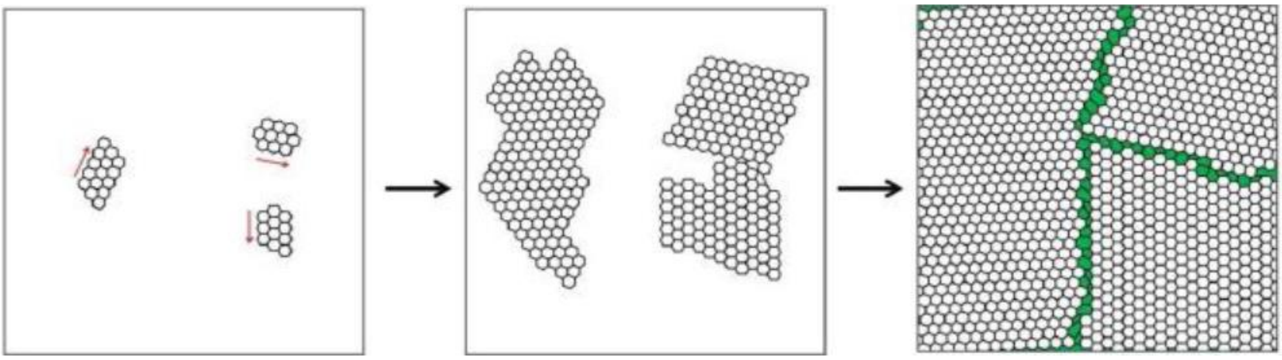


**Fig.4.** Schematic representation of the mechanism of graphene growth by CVD:
a) Carbon atoms; b) carbon atoms starting adsorption on the surface; c) growing separated graphene islands with same orientation; d) growing into the whole domain without defects on boundaries;

Ideally, a layer of graphene should formed, but as practice shows, the formation takes place in a semi crystalline order, this indicates individual islands of graphene with different orientations that begin to grow in unite, and then these boundaries form a semi crystalline structure. However, this structure cannot used in electronics due to lack of uniformity (Fig.5).



a) b) c)

**Fig.5.** The formation of polycrystalline graphene:
a) Formation of graphene islands with different orientation; b) graphene islands are spread out; c) growing into the whole domain with defects on boundaries;

In connection with this, a technique for the growth of individual graphene crystals from nucleation was developed. PMMA (polymethyl methacrylate) used for nucleation [7]. At Institute Physics and Technology, the PMMA applied through a pattern mask by photolithography method, and then separate PMMA grains obtained, which then during the high-temperature process residual polymer evaporated and only grains remained during the decomposition of the polymer, that is, definitely oriented carbon points. Next was the process of synthesis. Separate graphene islands obtained in Figure 6.

Figure 6 shows SEM images of synthesized graphene arrays onto PMMA grains with thickness of 2 and 0.4 microns. It is clear seen irregular shaped graphene islands; however, there are some islands close to the hexagonal structure.

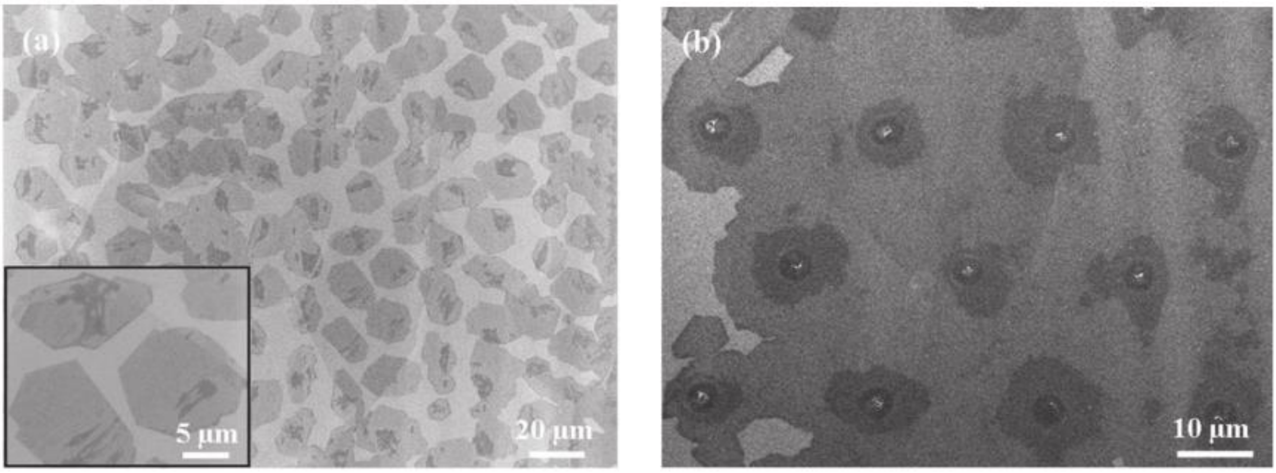


**Fig.6.** SEM image of graphene grains grown from PMMA grains on a copper substrate:
a) The thickness of PMMA grains are 0.4 microns; b) the thickness of PMMA grains are 2 microns;

Obtained results can explained that mainly formation of polycrystalline, which consist of several grains. The dark areas on each island indicate to several single-layer graphene domains, which formed due to solid carbon precursor (PMMA). As increasing the PMMA grains thickness to 2 microns (Figure 6b) at the same CVD synthesis process, the formation of graphene layer continuously in several layers of domains. Residual PMMA clearly observed on the image as white dots. By controlling the amount of PMMA, growth of graphene films with bi- or more layers become achievable.

## Conclusion

New materials based on graphene are promising in photocatalytic systems and gas sensors application. Due to the unique properties of graphene, it is possible to improve the photocatalytic characteristics by introducing it into various semiconductor photocatalysts. Such as adsorption, capacity and electrical conductivity will increase at extended light absorption range [9]. The role of graphene considered as a mediator for electron transfer, which leads to efficient separation of photo generated electron-hole pairs and improving photocatalytic performance. Moreover, it noted that graphene could also effectively used as a substitute for noble metals (such as Pt) in the photocatalytic decomposition of water [10].

In further study will develop hybrid multilayer heterostructures based on graphene, 2D-TMD layers, and nanoparticles, which will deposit or grown on graphene layers using various techniques for further investigation of their electrical and optical characteristics. Heterostructures based on graphene has a great opportunity in various applications.

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