Liquid Phase Growth of the Graphene using Ga_xNi_{1-x} System as Catalys

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Abstract—Deposition of few-layer graphene films on dielectric substrate by using a novel Ga_xNi_{1-x} flux LPG (Liquid Phase Growth) method is demonstrated. The graphene films shape themselves as circular thin films. The influence of the ingredients in the Ga_xNi_{1-x} system on the quality of synthesized graphene is discussed, graphene with better quality is synthesised when the Ga content is 50%. In addition, a growth mechanism is proposed. The graphene LPG is based on a two-step process. The first step is the formation of Ga_xNi_{1-x} flux and dissolution of carbon atoms during temperature elevation, the second process is the segregation of the carbon as graphene film from Ga-Ni flux during temperature dumping. We think that Ga_xNi_{1-x} system plays a catalytic role. Scanning electron microscope (SEM) and Raman Spectra are used for characterizing the experimental graphene films.

Keywords-graphene; liquid phase growth; Ga_xNi_{1-x} system; metalic catalyst; circular

I. INTRODUCTION

Graphene has been attracting great interest because of its ideal two-dimensional (2D) network with atomic scale thickness [1]. Single- and few-layer graphene films show excellent and unique physical properties, such as extraordinary high carrier mobility and the quantum Hall effect [2–9]. The mechanical flexibility and high optical transparency of graphene films are useful for flexible electronics [10–12] and their high surface area can be applied to sensors [13-15]. The excellent characteristics of graphene motivate lots of researchers to seek high performance growth method such as mechanical cleavage, ultrahigh vacuum annealing of single-crystal SiC (0001) and chemical method. However, above methods have this or that shortcomings. For example the mechanical cleavage method may lead to small areas coverage and the ultrahigh vacuum annealing of single-crystal SiC may lead to relatively high cost. Chemical vapor deposition (CVD) of hydrocarbon ingredients over transition metal films has been recognized as a promising method to synthesize large-area graphene films with low cost [16–19] in recent years. However, such approach with transfer step of graphene, usually deteriorates graphene properties by bringing in wrinkles and dislocations. Recently, researchers are working on achieving graphene without transfer step [18] to minimize the possibility of deteriorating graphene properties. In this paper, we tried a Ga_xNi_{1-x} system as catalyst for graphene LPG growth. This is the first time of using the Ga_xNi_{1-x} co- catalytic system in graphene growth process and no studies over such metal flux system have been reported for us to know to present. Besides the catalytic effect, another worth meeting fact is that the Ga-Ni co-solution partly evaporates during high temperature process, leaving the graphene standing on dielectric substrate or above less residual metal, which is nearly free-standing and easy to separate. Moreover, the graphene are circular thin films. Here, the Ga-Ni ratio is concerned. It creates a convenience for application where circular graphene is needed. At last, the mechanism of growth procedure is proposed combined with the shape of graphene. It is of great importance for controllable growth of graphene.

II. EXPERIMENTAL

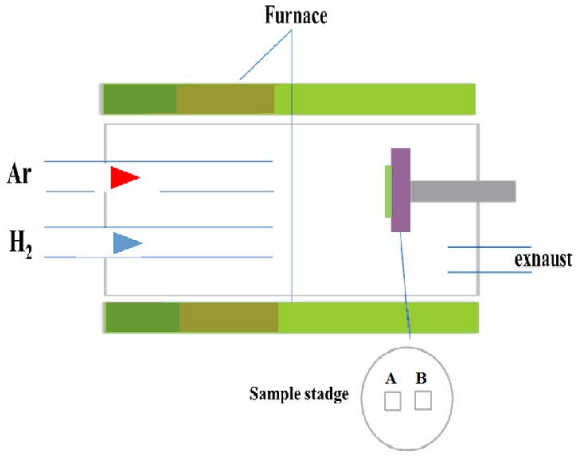


Figure 1. Drawing of the LPG system

The graphene films were synthesized in the device as shown in Fig. 1. At preparation step, two silicon wafers with 300 nm thick SiO_2 on top were chosen as substrates, which were marked as sample A and sample B. For sample A, a 300 nm nickel (Ni) film was deposited by electron beam evaporators, then 7 nm amorphous carbon layer used as carbon source was added on the Ni surface by vacuum sputtering. For sample B, 0.4 cm^3 of liquid gallium (99.9999 atomic% purity, Mining & Chemical Products) was dropped on the Si/SiO_2 surface which works as gallium source of the flux. The experiments were carried out in following procedure: First, the temperature was increased to 900°C at a speed of 180 °C/min, since 900°C is far beyond the melting point of Ga, gallium atoms on sample B evaporated, and a Ga-Ni flux is formed on the surface of sample A. Besides, carbon atoms seeped into the Ga-Ni flux. The next step is annealing, samples A and B were annealed under Ar/H_2 flow for 20 min at 900°C. During this period, the Ga-Ni flux dewets and partly evaporates, graphene film is formed. Finally the growth was terminated by cooling the samples to room temperature at a rate of 10°C/min.

III. Results and Discussion

Few-layer graphene films shaping themselves as circular thin films can be found in localized areas. As shown in Fig. 2a, the areas of the circular graphene films vary from 10 um to 300 um in diameter. Fig. 2b is the enlarged SEM image of the circular shaped graphene. It can be found that the contact between graphene grown by Ga_xNi_{1-x} LPG and the residual Ga-Ni metal is not that close as the traditional method. The circular graphene is more like free-standing as a collapsed balloon on the residual metal. This can be further confirmed by the inset in Fig. 2b, which makes the transferring of graphene to other target substrate much easier. The method for transferring graphene widely uesd today is soaking the sample in $FeCl_3$ or $FeNO_3$ solution for more than 10 hours to etch away the metalic catalyst. Such a transferring process costs much time and increases the number of defects in graphene film. On the contrary, graphene synthesized in this paper on residual metal surface is very easy to be transferred. They can be separated from the substrate using ultrasonic washing in deionized water for 30 seconds, then the graphene films can be salvaged with target substrates. Fig. 2c shows the graphene morphology after deposition on target substrate. It can be seen that the graphene films kept circular shape and no obvious cracks were found. Fig. 2d shows that after transferring process, the residual metal beneath the graphene keeps the same as before, which confirms that none etching solution is used in such process.

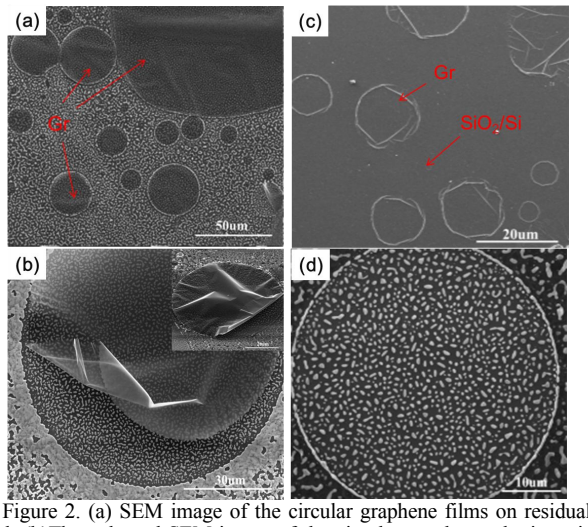


Figure 2. (a) SEM image of the circular graphene films on residual metal; (b)The enlarged SEM image of the circular graphene, the inset is SEM image of the circular graphene rotated 40°; (c)SEM image of the circular graphene after transferring to target substrate; (d)SEM image of the residual metal after graphene transferred away.

As for the graphene film formation and the reason why these graphene shaped themselves as collapsed balloons, the discussion is below.

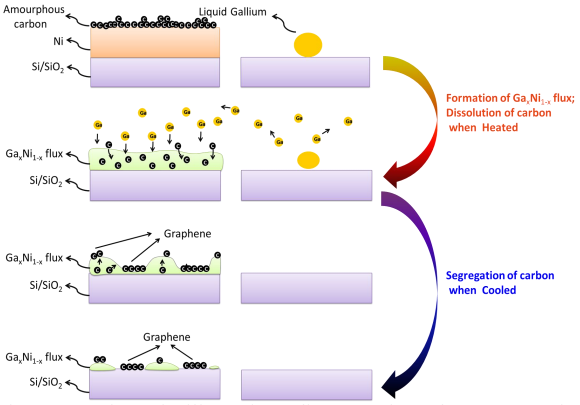


Figure 3. Schematic illustrations diagram of graphene LPG using liquid gallium as a flux.

We consider a possible growth mechanism for the LPG process using Ga_xNi_{1-x} flux as shown in Fig. 3. The graphene LPG is based on a two-step process. The first step is the formation of Ga_xNi_{1-x} flux and dissolution of carbon atoms during temperature elevation. When the sample was heated, C-C bonds in amourphous carbon film were broken and the carbon atoms dissolved into the Ni metal. At the same time, Ga atoms evaporated from the liquid Ga drop combine with Ni and formed Ga_xNi_{1-x} flux. The key point is application of gallium whose melting point is only 29.8°C, which resulted in the Ga_xNi_{1-x} system melting at a much lower temperature.

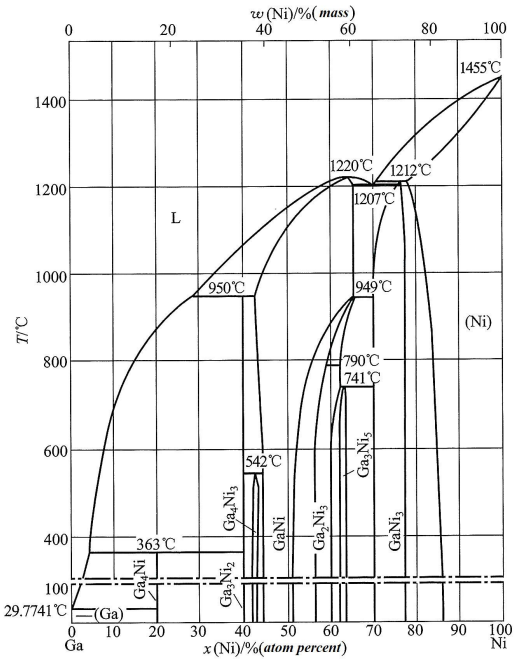
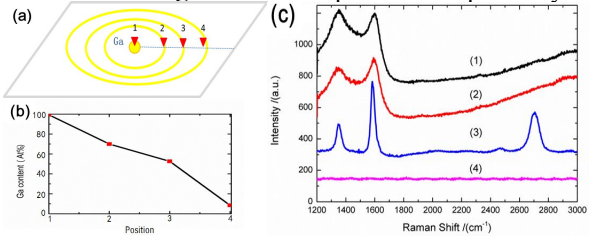


Figure 4. Binary alloy phase diagram of Ni-Ga.

And the fact can be derived from the phase diagram of Ga-Ni co-system (Fig. 4). The second process is the segregation of the carbon as graphene film from Ga-Ni flux during temperature dumping. In this process, we think that Ga_xNi_{1-x} system plays a catalytic role. In the process of graphene film formation, the amorphous carbon acts as a supplier of carbon, while the Ga_xNi_{1-x} flux serves as a catalytic temporal reservoir of carbon.

The elliptical shape of graphene flakes achieved in our experiment might be caused by the ingredient of metal catalyst. For further illumination the graphene elliptical form evolution process and to study the influence of proportion of Ga and Ni on graphene growth, another experiment has been conducted. A drop of liquid Ga(0.4 cm^3)was dropped in the center of a Si/SiO_2 substrate with 300 nm nickel (Ni) film on the surface and then 5nm amorphous carbon film was sputtered on it. The sample was then annealed at 900°C for 20 min. EDXS was used to detect Ga composition at various positions and the result indicates that the content of Ga reduces gradually along the radial direction. We selected 4 locations in the sample for SEM and Raman spectroscopy characterization as shown in Fig. 5. The morphology of Ga drop is shown in Fig. 5d which correspond to position 1 (99%Ga). Position2, 3, 4 represent relatively high level of Ga content (70%Ga), middle level of Ga content (50%Ga), and low level of Ga content (8%) respectively. Fig. 5c shows the Raman spectroscopy images of the four positions. Fig. 5d, 5e, 5f, 5g are the SEM images of the four positions respectively.



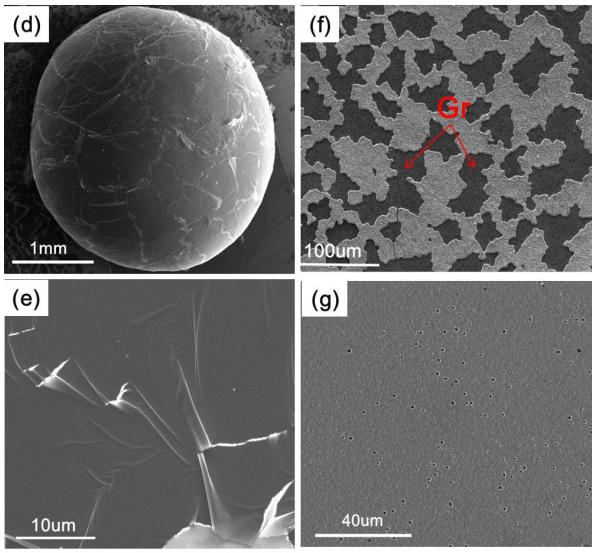


Figure 5. (a)、(b) Ga content at position1, 2, 3, 4; (c) Raman Spectra from position 1, 2, 3, 4；(d)、(e)、(f)、(g) SEM images of the position 1, 2, 3, 4 respectively.

Two key points can be concluded according to above experimental results:

1) The shape of graphene film synthesized is associated with the Ga proportion. In position 2 (70%Ga), the metal was almost completely evaporated and the graphene films were grown directly on a Si/SiO_2 substrate (Fig. 5e). In position 3 (50%Ga), the Ga-Ni flux was partly evaporated and some holes with area of about $20um^2$-$100um^2$ are found (Fig. 5f) and graphene flakes of micron scale size are obtained in the hole area on the bare Si/SiO_2 substrate. Besides, preceding circle-shaped graphene film is dominatly observed with the morphology as shown in Fig. 2. While for position 4 (8% Ga) the metal film keeps almost complete without graphene (Fig. 5g). As we know, the Ga_xNi_{1-x} co-solution was keeping dewetting and evaporating at elevated temperatures. Due to metal evaporation during temperature dumping in some places, the Ga_xNi_{1-x} system agglomerate into hemispherical droplets. Carbon atoms segregate onto the surface of the droplet and form elliptical appearance. In this case, the half spherical droplet works as a mold, graphene film synthesized would replicate the hemispherical shape of the droplets. In this case, after the Ga-Ni metal droplet was evaporated, and the graphene would shape itself as a collapsed balloon on the residual metal (as shown in Fig. 2)
2) The quality of Graphene synthesized is also associated with the Ga proportion. We can see that from Fig. 5c, graphene with better quality is synthesised when the Ga content is 50%. For other positions with Ga content higher or lower than 50%, the quality of graphene declines.

IV. CONCLUSION

In this work, we propose and demonstrate, for the first time, the use of Ga_xNi_{1-x} system as the sacrificing layer and catalyst for graphene film growth by LPG method on a single-crystal substrate. Above target substrate, we

achieved graphene films shaping itself as a collapsed balloon on the residual metal. That may be a shortcut for tailoring graphene into circular shape. Besides, the free-standing graphene synthesized here is very easy to be transferred to other target substrates using simple ultrasonic washing, since the formed graphene is non-contact or nearly free-standing on the residual metal. A mechanism for circular shaped graphene evolution process is proposed, while, the influence of Ga_xNi_{1-x} system on the size of graphene still needs further investigation, which is important for quality optimization.

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