Chemical vapor deposition growth and characterization of graphite-like film

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Abstract

Thick graphene film can be widely used in surface protection, heat dissipation, heating devices and other fields. Here we present a study on the growth and characterization of large area continuous and patterned graphite-like films prepared on Ni foil through CVD. Effects of parameters on the material growth are studied experimentally and theoretically in detail. Thickness of the graphite-like film in this work can reach 500 nm and can be regulated by growth process. Characterization results show that the graphite-like film is formed by free stacking of large area graphene continuous films and possesses strong mechanical strength, chemical stability, good electrical conductivity and flexibility. The graphite-like film shows potential for application in metal surface protection, flexible conduction, heating and electromagnetic shielding.

1. Introduction

Graphene has attracted considerable interest because of its unique properties and potential applications [1–3]. Graphene grown by CVD has obtained great attention because of the ease of growing large-area continuous films on metal substrates, such as Cu [4–13] Ni [14–17], and Pt [18]. At present, graphene prepared by CVD is mostly monolayer [4–10], with few layers (usually within three) [14–17, 19] and exhibits satisfactory flexibility, transparency, and high mobility. However, this type of graphene is very thin and thus has poor mechanical strength, heat conduction, and conductivity, which hinder their application in heat dissipation, metal protection, and other fields. For example, graphene has been predicted to act as protective membrane because of its good thermal and chemical stability [20–22]. In previous articles, scholars have reported the excellent performance of graphene on metal substrates in terms of resistance to oxidation and corrosion [23–27]. By contrast, subsequent reports found that monolayered graphene cannot protect the metal at high temperatures or for a long time because the defects, such as grain boundaries and wrinkles in graphene [28–32]. The level of graphene protection against metals will be greatly enhanced if the number of graphene layers is increased. In previous studies, multilayered graphene domains have been obtained on liquid Cu [13] and Ni [17] substrates, but few thick (more than 10 layers) continuous films have been prepared.

In this work, large area continuous and patterned graphite-like films on Ni foils were prepared through hot CVD. The structure and stacking mode of the graphene layers in the graphite-like film were clarified through high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) analyses. The transport process of carbon atoms in the inner portion and surface of Ni substrate was investigated through theoretical calculations to elucidate the mechanism of the growth of graphite-like films on Ni foil. Experimental results show that the graphite-like film possesses significantly increased mechanical strength and
can be easily transferred without glue. The protective ability of graphite-like film on the material surface is greatly improved compared with that of single-layered graphene. The electrical conductivity of the graphite-like film is better than that of single-layered graphene by more than two orders of magnitude. Although the thickness increases, the graphite-like film retains its good flexibility. The graphite-like films were then employed as flexible electrode and heating device.

2. Experimental section

Growth of the graphite-like film with CH$_4$ as carbon source. The graphite-like films were prepared on the Ni foils in a quartz-tube furnace under ambient pressure. The purity and thickness of the Ni foil in our experiment were 99.99% and 150 μm, respectively. Before growth, the Ni foils were washed with acetone and deionized water. Cleaned Ni foils were heated to growth temperature under 800 sccm Ar and 200 sccm H$_2$, and then CH$_4$ was introduced to start growth. After growth, the Ni foils were cooled down in the protection gases.

Growth of the Patterned graphite-like Film with graphite powder as carbon source. The Ni foil and the clean graphite powder to make graphite mud, and then a tweezers was used to dip the graphite mud and paint patterns on the upper surface of cleaned Ni foil. Heating the patterned Ni foil to growth temperature under 800 sccm Ar and 200 sccm H$_2$, held for 30 min, and cooled down.

Sample charaterizations. Zeiss Super 55 scanning electron micrograph with 3 kV voltage was used to collect SEM images. A JEM-2100F field emission TEM with an acceleration voltage of 200 kV was used to collect HR-TEM images. Raman spectra were detected by a Thermo-Fisher DXR 532 nm Filter Micro-Raman system. AFM (Veeco Multimode V) was conducted at room temperature. The electrical resistance was measured by a four-probe technique using a physical property measurement system (Quantum Design, PPMS).

Computational details: all calculations with the density functional theory (DFT) approach were performed using projector augmented wave (PAW) method as implemented in the Vienna ab initio Simulation Package (VASP). The electronic exchange-correlation energy was treated by the generalized-gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE). The energy cut off for the plane-wave expansion was set to 450 eV. The k-point sampling in the Brillouin zone was implemented by the Monkhorst-Pack scheme with the grids of $4 \times 4 \times 1$, $6 \times 6 \times 1$, and $4 \times 4 \times 1$ for Ni(100), Ni(110), and Ni(111) supercells, respectively. The climbing-image nudged elastic band (CINEB) method was used to determine the energy barriers and minimum energy paths (MEPs) for the migration in the surface and subsurface of Ni substrates. All Ni surfaces were modelled by using slab geometry with six atomic layers in which the bottom-bilayer atoms were fixed at their bulk positions. The unit cells of the slabs are 12.46 Å × 12.46 Å, 10.57 Å × 9.97 Å, and 10.79 Å × 12.46 Å for Ni(100), Ni(110), and Ni(111) surfaces, respectively. These Ni surfaces with in-plane periodicity were separated by a ~15 Å vacuum layer to prohibit the interactions between neighboring slabs. All these structures were relaxed until the total energy and forces acting on each atom were less than 10–5 eV and 10–2 eV/Å, respectively.

3. Results and discussion

3.1. Growth and transfer of continuous graphite-like film

Figure 1(a) shows the schematic of graphite-like film growth process on Ni substrate. First, CH$_4$ is decomposed at high temperature, and the decomposed carbon atoms are then integrated into the Ni substrate. When cooling down, the carbon atoms precipitate from the substrate and form graphene on both sides of the substrate. With continuous cooling, the carbon atoms continue to precipitate, a new graphene layer is formed between the graphene and the substrate, the number of graphene layers gradually increases, and the graphite-like film is eventually formed. The scanning electron microscopy (SEM) images in figures 1(b), (c) show the surface morphologies of graphite-like films at the upper and lower surfaces of Ni substrate, respectively. The graphite-like films on both surfaces possess obvious wrinkles with various sizes, and the areas outside the wrinkles appear smooth. The Raman spectra of graphite-like films on both surfaces present typical 2D and G peaks (figure 1(d)), indicating that the graphite-like films have graphene structure. The weak D peak means the high quality of the graphite-like films, and the smaller intensity ratio of 2D peak to G peak suggests the presence of many graphene layers in the graphite-like film. In addition, the Raman spectra of the upper and lower graphite-like films are similar, indicating that the films have similar quality and thickness. The measurement results of step profiler (figure S1 is available online at stacks.iop.org/MRX/7/015609/mmedia) show that the thickness of graphite-like films can reach 500 nm. The wrinkle morphology of the graphite-like film is determined by atomic force microscopy (AFM). It can be found that the shape and size of the wrinkles are various (figures 1(e)–(f)), and the height and width of bigger wrinkles can reach 100 and 300 nm, respectively. The distribution of wrinkles in the graphite-like film is related to the Ni crystal structure, and the additional AFM images are presented in figure S2.
Information related to graphite-like film transfer are shown in figure 2. Figure 2(a) shows the schematic of graphite-like film covering Ni substrate before and after FeCl₃ corrosion. Prior to corrosion, the Ni substrate covered with two graphite-like films can be divided into three parts of close combination. The blue area in the middle is the Ni substrate containing carbon atoms, and the upper and lower areas with dark colour are the graphite-like films. After Ni substrate is corroded (as indicated by the arrow), the upper and lower graphite-like films separate, and the carbon atoms in the Ni substrate lose support and reunite into thin films. Figure 2(b) shows the sample mentioned in figure 1 before and after corrosion. As shown in figure 2(a), three layers of the thin film are left after the corrosion of the Ni substrate. The films noted with 1 and 3 correspond to the upper and lower graphite-like films, respectively. The film noted with 2 is formed by dissolving carbon in the Ni substrate. The Ni substrate covered with graphite-like films is not glued before corrosion. Therefore, three films are suspended in the solution by their own mechanical strength after the Ni substrate is corroded. A large area of single-layered graphene typically needs to rely on the support of glue to float in the solution. Hence, the mechanical strength of the graphite-like film is far higher than that of the single-layered graphene. Figures 2(c), (d) show the SEM images of films 1 and 3 transferred on SiO₂. Various wrinkles with different sizes are found on the graphite-like film surface. The morphology of graphite-like film after transfer is similar to that before transfer (figures 1(c), (d). Figure 2(e) shows the SEM image of film 2. Figure 2(e) shows that the film 2 is not continuous and differs from films 1 and 3. Figure 2(f) shows the Raman spectra of the films in figure 2(b). Obvious 2D and G peaks are found in the Raman spectra of the upper and lower graphite-like films (films 1 and 3) and correspond to the graphene structure. The Raman spectra of film 2 have no 2D peak but only G and D peaks, demonstrating that film 2 has an amorphous carbon structure. The discovery of film 2 strongly proves that the growth mechanism of graphene on the Ni substrate involves dissolution and precipitation. To our knowledge, film 2 has not been found in previous reports on graphene growth.

3.2. Growth and transfer of patterned graphite-like films

Patterned graphite-like films are also grew on Ni foil using graphite powder as source. Figure 3(a) shows the schematic of patterned graphite-like film growth process on Ni substrate. Similar to the growth mechanism of continuous graphite-like films, patterned graphite powder is decomposed at high temperature, and the decomposed carbon atoms are then integrated into the Ni substrate. When cooling down, the carbon atoms...
Figure 2. (a) Schematic of graphite-like film-covered Ni substrate before and after FeCl₃ corrosion. (b) Photos of the Ni substrate covered with the graphite-like film (the sample mentioned in figure 1) before and after FeCl₃ (1 g l⁻¹) corrosion. (c)–(e) SEM images of the films in (b) noted with 1(c), 3(d), and 2(e). (f) Raman spectra of the films in (b). The bars in figures (c), (d), and (e) are 4, 4 and 200 μm.

Figure 3. (a) Schematic of patterned growth of the graphite-like on Ni substrate. (b) Photograph of a graphite pulp on the surface of Ni to form a letter G. (c) Photograph of the Ni foil in (b) after graphite-like growth. (d) Photograph of the Ni foil in (c) after the surface of the superfluous graphite powder shakes off. (e) Back photograph of the sample. (f) Photograph of the graphite-like film in (d) after transferring to SiO₂. (g) Photograph of the graphite-like film in (e) after transferring to SiO₂. (j) Photograph of the carbon film formed by dissolved carbon in Ni substrate. (i), (j) SEM images of the graphite-like films in d and e.
precipitate and form patterned graphite-like film eventually on both sides of the substrate. In addition, if the carbon source is excessive, there will be graphite powder residue on upper graphite-like growth of multiple graphene at one time. We explored the process of growing graphite-like functional theory calculations were performed to investigate the diffusion properties of C atoms on Ni substrates, the investigation of the diffusion behaviours of C atoms on different Ni facets will contribute to the understanding of facet-dependent layer thickness of graphite-like film, which indicates that the carbon atoms have also been transported laterally.

### 3.3. Key factors and mechanisms of graphite-like film growth

Effects of the substrate orientation and growth parameters on the graphite-like growth were studied in detail. Experiment results show that increasing the CH4 flow (figure S3), raising the growth temperature (figure S4), and slowing down the cooling rate (figure S5) can increase the growth rate of graphite-like film, and the crystal orientation of the Ni substrate has a significant effect on the growth of graphite-like film, the growth rate of graphene appears faster on the (111) facet of Ni grains (figure S6). In addition, to reduce the cost of graphene preparation, we explored the process of growing graphite-like films by stacking substrates and realized the growth of multiple graphene at one time (figure S7).

Considering that the formation of graphite-like film depends on the precipitation and diffusion ability of C atoms on Ni substrates, the investigation of the diffusion behaviours of C atoms on different Ni facets will contribute to the understanding of facet-dependent layer thickness of graphite-like films. Hence, density functional theory (DFT) calculations were performed to investigate the diffusion properties of C atoms on Ni (100), Ni (110), and Ni (111) surfaces. Figure 4 shows the diffusion pathways and the corresponding energy profiles of C atom diffusion on three different Ni substrates. On Ni (100) substrate (figure 4(a)), a smaller migrate barrier (~0.31 eV) of C atom from the subsurface to the surface (A → B) was observed, implying that the precipitation of C atom easily occurs on the Ni facet during the growth. By contrast, the diffusion barrier of C atom on Ni (100) surface (B → C) is very large (~1.32 eV). The result originates from the fact that the C atoms located at the hollow site of Ni (100) surface is very stable, resulting in a large diffusion barrier of C atom from a hollow site to another one. The large diffusion barrier of C atoms limits the rapid surface growth of graphene on Ni (100) surface. On Ni (110) substrate (figure 4(b)), the precipitation barrier of C atoms from the subsurface to the surface (A → C and B → C) is approximately 0.88–1.09 eV. Interestingly, we found that the diffusion barrier of C atom on Ni (110) surface strongly depends on the diffusion direction. As shown in figure 4(b), the diffusion barrier of C atom along the C → D direction is only 0.16 eV, but it increases to 1.14 eV along the D → E direction. The result implies that the graphene growth is highly anisotropic on Ni (110) substrate, which probably causes the formation of striped (or rectangular-like) graphene. On Ni (111) substrate (figure 4(c)), the diffusion barrier of C atoms from the subsurface to the surface (~1.06 eV) largely approaches that of the C atom on Ni (110) substrate. However, the C atom has a very small diffusion barrier (~0.29 eV) on Ni (111) surface,
which contributes to the rapid growth of graphene on Ni (111) surface. This is why the graphene domains appear on Ni (111) facets first in figure S6.

3.4. Structure characterization
High-resolution transmission electron microscope (TEM) and selected area electron diffraction (SAED) technique were used to investigate the interlayer distance and the angular relations among the graphene layers in the graphite-like film. Figure 5(a) shows the TEM image of partially folded graphite-like film transferred onto the Cu TEM grid. The TEM test requires electrons to pass through the sample, hence, we selected thinner samples for the test. The film in figure 5(a) is roughly divided into two regions: area 1 is the single-layered graphite-like film, and area 2 is the double-layered region formed by the folding of the single graphite-like film. The slash is the dividing line between the single- and double-layered graphite-like films. Figure 5(b) shows the SAED pattern of graphite-like film acquired on the circle region in figure 5(a). Similar to that of the single-layer graphene, the SAED pattern of the graphite-like films shows hexagonal diffraction spots. However, each diffraction feature has three diffraction spots, hence, the first-order diffraction feature is not a regular dot. The third-order diffraction feature splits into three distinct spots. The sharpness of the split spots clearly indicates the 2D crystallinity associated with the graphene layers. The angle between the split spots directly relates to the angle orientation between the graphene layers in the graphite-like film, and the intensity of each split spot depends on the number of participating layers with similar angular relation [33]. The high-resolution image of the rectangular area in figure 5(a) is shown in figure 5(c), in which the image of the stacked layers of graphene on the side of the graphite-like thin film can be clearly observed. From figure 5(d), the thickness of 14 layers of graphene is approximately 5 nm, therefore, the thickness of a graphene layer in the graphite-like film is approximately 0.36 nm. Figure 5 shows that the graphite-like thin film is formed by free stacking of multi-layered high-quality graphene, and the thickness of graphite-like film with thickness above 400 nm should contain more than 1000 layers of graphene.

3.5. Application demonstrations of graphite-like Film
The performance of graphite-like films as Cu anti-oxidation protection film was measured and compared with the performance of graphene (in situ grown on Cu foil, mainly single layer), the results are shown in figure 6. The inset in figure 6(a) shows a photograph of graphite-like film grown on Ni transferred to Cu foil, in which the gray area at the left upper portion is the graphite-like film covered Cu surface, and the other area is the exposed Cu surface, which is slightly oxidized to brown color due to contacting with water during the graphite-like film transfer process. From figures 6(a)–(c), there is no obvious change in the graphite-like film covered Cu surface after annealing at 250 °C, 350 °C, and 450 °C for 30 min in air, respectively. However, the single layer graphene...
covered Cu surface shows the obvious changes after annealing. As mentioned in our previous report [30], obvious oxidized lines were observed after annealing at 250 °C for 30 min (figure 6(d)). From figure 6(e), after annealing at 350 °C for 30 min, partially graphene covered Cu surface was completely oxidized (brown area), and the oxidation degree of the Cu surface in the white area was weaker. After annealing at 450 °C for 30 min (figure 6(f)), the whole Cu surface changed to brown, which indicates that the whole Cu surface was severely oxidized. The oxide Cu layer in some severe oxidation regions is relatively thick, due to the stress the oxide layer and the Cu foil below are separated and formed obvious uplift (noted with arrow). Figure 6(g) shows the photograph of samples after annealing at 550 °C for 30 min. In the area of exposed Cu surface (noted with 2) and graphene-covered Cu surface (noted with 3 and 4), large area CuO layers began to separate and shed from the Cu foil. However, no obvious change was observed in the graphite-like film covered area (noted with 1), and the optical image (figure 6(h)) also shows that the graphite-like film covered Cu surface remained unchanged. Figure 6(i) shows the Raman results of the graphite-like film covered Cu surface before and after annealing at 550 °C and the exposed Cu surface after annealing at the same temperature. From figure 6(i), we can see that both 2D and G peaks of the graphite-like film do not show obvious change before and after annealing, and no CuO or Cu2O peaks were observed. However, the peak corresponding to Cu2O was observed at 419 and 628 cm⁻¹ for the exposed Cu surface. Figure 6 demonstrates that graphite-like films can be kept stable at 550 °C in air, and the Cu surface underneath is well protected from oxidation. The results of the comparison tests prove that the performance of graphite-like film as Cu oxidation protection film is far better than that of monolayer graphene. The resistance to hydrogen etching (figure S8) and the performance of graphite-like film as metal anticorrosion protection film (figure S9) were also evaluated. Results show that the graphite-like film has a strong ability to resist hydrogen etching and can effectively block liquid reagents, as well as to protect metals.

Graphite-like films can be utilized as heating devices considering their excellent stability and conductivity. In order to avoid external damage, a graphite-like film and two thin (25 μm) Cu foils were sealed in two slide glass to make graphite-like glass. As schematically shown in figure 7(a), the graphite-like film and the Cu foils were sandwiched between two pieces of glass, heated to 750 °C in argon, the edges of the two pieces of glass stick
Figure 7. Performance of graphite-like glass as a heating device. (a) Schematic of the heating device constructed with graphite-like film and glass. (b) Photograph of the graphite-like glass heating device. IR photographs of graphite-like glass before (c) and under (d) an input voltage of 3.75 V. (e) The 3D picture of (d). (f) Temperature of the graphite-like glass under different input voltages.

Figure 8. (a) Photograph of graphite-like film transferred to PET. Picture of the graphite-like/PET as a flexible wire before (b) and after (c) electricity. (d) Picture of the heavily curved graphite-like/PET as a flexible wire after (c) electricity (e). Magnified picture of the graphite-like/PET in image (d).
together. Figure 7(b) shows a photograph of the graphite-like glass on a culture dish. The gray area in the blue square frame is the graphite-like film, and the long strips of Cu on both sides are electrodes. The glass is slightly deformed after high temperature. An extended-range IR camera was used to map the surface temperature of sample. The initial surface temperature for graphite-like glass is firstly measured to be equal to the environment temperature ∼26 °C (figure 7(c)). By inputting a safety DC voltage (3.75 V) to the device, the surface temperature of graphite-like glass reaches ∼240 °C (figures 7(d)–(e)). Figure 7(f) displays the curve of surface temperature of the graphite-like glass as a function of applied voltage. Notably, a higher applied voltage results in a higher surface temperature of the graphite-like glass.

The electrical measurement results show that the square resistance of 500 nm graphite-like film is less than 1 Ω sq−1, which is approximately two orders lower than that of single graphene. The temperature-dependent resistances of the graphite-like film and monolayer graphene with the same size are measured, and the results are shown in figure S10.

The graphite-like film was also transferred to the PET substrate as a flexible conductive film. The picture of the graphite-like film transferred to the PET substrate is shown in figure 8(a), in which the blue box is the edge of the PET substrate and the gray area in the box is the graphite-like film. From figures 8(b) and (c), we can see the graphite-like/PET film (noted with the arrow) acts as a flexible wire in a circuit with a small bulb. After the circuit is connected, the small light bulb is bright. After heavily curving, from figures 8(d), (e), the small light bulb is still bright, which indicates that the graphite-like/PET film is conducting after heavily curving, and repeated bending 200 times does not significantly change the conductivity of graphite-like film.

4. Conclusion

In summary, we have demonstrated the growth of graphite-like film on Ni foil through CVD. It is easier to obtain uniform continuous graphite-like films by using methane as carbon source, while patterned graphite-like films can be obtained by using graphite powder. In addition to the films on the upper and lower surfaces of the substrates, an amorphous carbon film was obtained, which indicates that the growth mechanism of the graphite-like film is dissolution and precipitation. Increasing the growth temperature and carbon source concentration is beneficial to increasing the film thickness. The theoretical calculation results show that the growth rate of graphite-like films on the substrate (111) surface is the fastest. The SAED pattern shows that the graphite-like film is formed by free stacking of high-quality graphene layers. The graphite-like film possesses strong mechanical strength and can be easily transferred without glue. The chemical properties of the graphite-like films are very stable, it can protect Cu surface from oxidation in 500 °C air and protect the Cu surface from FeCl3 corrosion. The graphite-like films also have good conductivity and flexibility, the graphite-like films were employed as flexible electrode and heating device.

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