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Wrinkle-dependent hydrogen etching of chemical vapor deposition-grown graphene domains

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ABSTRACT

Hexagonal single-crystal graphene domains were grown on copper (Cu) foil via chemical vapor deposition and were etched with hydrogen at 950 °C from 7 to 60 min at atmospheric pressure. Numerous trenches were observed on the initial graphene domains after etching, and the trench patterns were closely associated with the Cu crystal orientation. No trenches were found if the etching process was conducted before cooling down. Thus, the etching trenches were bound up with the wrinkles formed during the cooling down process. Then, the process of etching on the wrinkles was examined. This simple hydrogen etching technology proved that wrinkles and point defects existed even in hexagonal single-crystal graphene domains. This method could be a convenient way to detect the distribution and morphology of wrinkles in graphene.

1. Introduction

Given its interesting physical properties [1–3], graphene has drawn significant attention as a novel two-dimensional system with significant potential in future electronic and optoelectronic applications [4,5]. Compared with other graphene synthesis processes, graphene grown on copper (Cu) substrates via chemical vapor deposition (CVD) has the distinct advantage of providing extremely large-area graphene films transferable to other substrates for graphene electronics with compatible wafer-scale fabrication.

However, carrier mobility in CVD graphene is less than that in exfoliated graphene [6–9]. Several studies have reported the effect of grain boundaries [10–13] in continuous CVD graphene on its electrical property. Improvements in growth techniques have led to large-scale grain sizes, which may enhance the electrical property of graphene. Meanwhile, the effect of wrinkles in continuous graphene films on electronic transport was reported by Zhu et al. [14].

Sub-millimeter single-crystal graphene has been synthesized [15] and meets the size requirements of typical sub-micrometer graphene devices. For large-domain films, the effect of grain boundary on electrical property can be reduced. Li et al. [16] reported that the electron mobility of the large-domain films extracted from field-effect transistor measurements was approximately 4000 $cm^2 V^{-1} s^{-1}$. However, this electron mobility is still less than that in exfoliated graphene. Thus, the electronic transport in the large graphene domain is also affected by other factors such as point defects and wrinkles.

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In this study, hexagonal single-crystal graphene domains were grown on copper foil via CVD and were etched with striated and reticular trenches by exposing the graphene to hydrogen flow at high temperatures. The etching pattern was found to be wrinkle-dependent. This simple hydrogen etching technology proved that wrinkles and point defects existed even in hexagonal single-crystal graphene domains, and that this method might be a convenient way to detect the distribution and morphology of wrinkles in graphene.

2. Experiment

Graphene was synthesized by using copper foil (99.9%, 2 cm × 2 cm strips) as a substrate. Copper foil was loaded into a 2 in fused quartz tube and heated to 1050 °C with flow of 1000 sccm Ar at atmospheric pressure. The Cu foil was then annealed at 1050 °C for 60 min with 1000 sccm Ar and 200 sccm H_2. After annealing, 500 sccm Ar, 20 sccm H_2, and 1 sccm dilute CH_4 (mixed with Ar) were introduced to the CVD system for 60 min for graphene growth. Then, the furnace was switched off and allowed to cool to room temperature under the Ar gas flow. Thermal hydrogen etching of graphene was conducted with flow of 500 sccm Ar and 200 sccm H_2 at atmospheric pressure, and etching was performed at 950 or 1050 °C.

3. Result and discussion

As shown in Fig. 1a, hexagonal single-crystal graphene was synthesized following a copper-catalyzed CVD method by using methane as carbon source. After the morphological testing of graphene, the samples were placed into the growth chamber again, and H_2 etching of graphene was conducted at 950 °C with a 2:5 hydrogen–argon (Ar) gas flow rate at atmospheric pressure.

Reaction time typically has a significant function in chemical reactions. To observe the etching process better, we studied the influence of etching time on the graphene etching reaction. A series of graphene etchings on the copper foils were conducted at incremental time intervals of 7, 20, 60, 240, and 360 min. Fig. 1b presents the optical microscope image of the hexagonal single-crystal graphene on the copper surface after 7 min of etching. The etching is wild and random. Only a small amount of etched trenches are observed in the hexagonal single-crystal graphene. These etched trenches appear narrow and sparse; they are several tens of nanometers wide and several tens of micrometers long.

Figs. 1c and 1d show images of the graphene crystal for etching at 20 and 60 min, respectively. The etched trenches increased in density and width with time, and the percentage of etched graphene was higher, which resulted in the formation of graphene islands in the single-crystal graphene domain. The hexagonal shape was maintained over the full range of domain sizes, and the crystal was not deformed by etching. When the etching time was further increased to 240 min, the single-crystal graphene was etched away, which left a hexagonal shape on the copper surface, as shown in Fig. 1e. No signal of G or 2D band in the Raman spectrum was detected, which indicated that the entire hexagonal graphene had been etched away. As the etching time increased to 360 min, the etched hexagonal shape on the copper surface became unsharp because of the reconfiguration of the copper surface, as shown in Fig. 1f.

Scanning electron microscopy (SEM) was conducted to obtain the morphology of several differently shaped graphene domains (hexagonal, star, and rectangular shapes) directly on the surface of the copper foils, and a similar pattern of etching trench was observed in different domains, as shown in Fig. 2a–c. All of the trench patterns in these graphene domains had a reticular structure, and the density and width of the etching trench appeared to be in the same order of

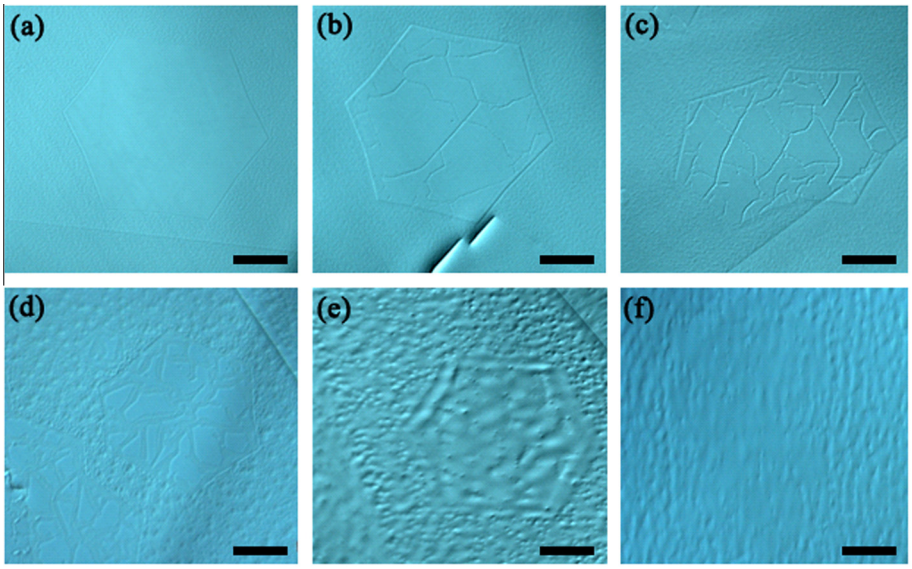

Fig. 1 – (a) Optical microscope images of graphene before etching. (b–f) Optical microscope images of the degree of corrosion depending on the etching time of 7, 20, 60, 240, and 360 min. The scale bar is 20 μm. (A colour version of this figure can be viewed online.)