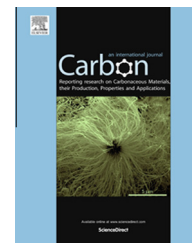


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# Combined effects of hydrogen annealing on morphological, electrical and structural properties of graphene/r-sapphire

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## ABSTRACT

We proposed a comprehensive study on the combined effects of hydrogen thermal annealing process on the morphological, structural and electrical properties of graphene transferred on r-plane sapphire (1–102). We found that although thermal annealing can remove the polymeric residues, unintentional p-type doping of polymeric residues and structural breakages arise simultaneously with the in-plane tensile strain. Also, the forming mechanism of cracks and p-type doping effect were investigated through Raman spectroscopy, atomic force microscopy, non-contact Hall and high resolution X-ray photoelectron spectroscopy. It revealed thermal annealing process has a combined influence on the performance of the hydrogen annealed samples with a critical point, which was  $\sim 250$  °C in this work. When the annealing temperature was over the critical point, significant p-type doping effects were included in a dominant position because of graphene with in-plane strain. The results can be important for the fabrication or chemical processing of graphene-based materials and devices.

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## 1. Introduction

Due to its outstanding electrical and optical properties, graphene has attracted increased attention for use in low-noise super-high frequency transistors, transparent conductive electrodes, biosensors and energy-storage devices [1]. Chemical vapor deposition (CVD) plays an important role in the fabrication of large-scale uniform graphene [2–4]. The unique two dimensional properties of graphene makes it an ideal candidate for device fabrication because graphene can be transferred onto arbitrary substrates such as SiO<sub>2</sub>/Si, glass, quartz, sapphire and PET [5–10]. However, the resist polymer,

which acts as a supporting substrate during the catalyst metal etching and transferring to desired substrates, cannot be entirely removed during the fabrication and chemical modified processing [11–13]. Even after 24 h of dissolving in acetone or other solvents, there may still be a layer of polymeric residues left on the surface of the transferred graphene. This will unavoidably hamper the electrical performance of the transferred graphene, with effects such as unintentional doping, morphological damage and other performances degradation [14–16]. For obtaining a clean graphene surface and improving the potential for applications of the graphene based materials and devices, much focus has been placed

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on the polymeric residue removal by thermal annealing in vacuum or forming gases; hydrogen, nitrogen, argon or a mixture of the two [14,17–19]. Thermal annealing processes have been investigated as an essential method in the fabrication of graphene-based devices; including the removal of surface polymeric residues, metallization for perfect contact of metals to graphene and modulation of the charge-conductivity [20–23]. A spanning range of thermal annealing temperatures and conditions have been reported, with corresponding contributions of unintentional doping and in-plane strain. However, these previous efforts focused independently on the removal of polymeric residues or electrical doping. The structural damages of the in-plane strain arising from the thermal treatment are seldom discussed, much less a combined influence of properties of graphene-based materials and devices. In attempts to make clear the mechanism of the thermal annealing process, it is necessary to perform a deep and systemic study on the joint influence of the thermal annealing process.

In this work, we present a systemic investigation on morphological, electrical and structural performance of hydrogen thermal annealed graphene/r-sapphire in a low pressure furnace tube. The reason we chose the r-plane sapphire as a target transferred substrate was the r-sapphire substrate is not only dielectric and non-polar, but also has perfect surface morphology, making it an attractive candidate for substrates in semiconductor and electrical devices [9,24]. The surface morphology of hydrogen annealed samples was measured by atomic force microscope (AFM), optical microscopy and high-resolution scanning electron microscopy (SEM). The electrical properties of the as-transferred and annealed samples were carried out by a non-contact Hall system using microwave probing at room temperature. The electrical doping and structural damages of in-plane strain from the thermal mismatch between graphene and substrates were determined by Raman spectroscopy. We also focused on the alteration of chemical bonds during the thermal annealing by high resolution X-ray photoelectron spectroscopy (XPS). Furthermore, the forming mechanism of a combined effect of the removal of polymeric residues, unintentional p-type doping and the structural damages arising from the in-plane tensile strain is deeply discussed throughout the whole article.

## 2. Experiments

The copper foil (25  $\mu\text{m}$  thickness, Alfa Aesar, No. 46365, purity of 99.8%), used as a catalyst in a low pressure chemical vapor deposition (LP-CVD) system to decompose methane, is a polycrystalline Cu foil with an average grain size of about 1 mm. The Cu foils were first etched for 1 min in  $(\text{NH}_4)_2(\text{SO}_4)_2$  solution (0.1 mol/L) and then cleaned by de-ionized water, analytical reagent ethanol and dried by high purity nitrogen. The Cu foils were pre-annealed for 1–2 h in high purity hydrogen with a gas flow rate of 100 sccm to achieve a higher quality of Cu surface morphology. A desired amount of super-high purity methane was introduced into the quartz furnace tube, and the methane partial pressure was controlled by a gas flow controller (partial pressure is 6–8 Pa in our CVD system). Large-scale monolayer graphene was synthesized by LPCVD at a typical temperature of 1060  $^\circ\text{C}$  for 30 min, with a total

pressure of about 200 Pa. During the growth and cooling process, a gas mixture of super-high purity methane and hydrogen were continuously passed through the furnace. The flow rate and pressure were also kept invariable. Finally, the furnace was cooled down rapidly with a cooling rate of 15  $^\circ\text{C}/\text{min}$ . The as-grown graphene samples were then transferred onto r-plane sapphire substrates by a common transfer method by polymethyl-methacrylate (PMMA, Microchem,  $M_w = 495 \text{ K}$ , C4) supporting, with a PMMA thickness of 100  $\mu\text{m}$  [2]. The Cu underneath foils were first etched for 3–4 h in  $(\text{NH}_4)_2(\text{SO}_4)_2$  solution (0.1 mol/L) and then cleaned by de-ionized water, analytical reagent ethanol and dried by high purity nitrogen. The supporting PMMA was dissolved by analytical reagent acetone for 12 h and ethanol for 1 h. Next, the as-transferred samples were hydrogen annealed for 2 h with a gas flow rate of 10 sccm and temperature ranges of 100–500  $^\circ\text{C}$  in a low pressure quartz furnace tube.

The surface morphology measurement of the as-transferred and the hydrogen annealed samples were carried out by atomic force microscope (AFM) (Veeco, NanoScope III) in a tapping mode. The quality and the layer's number of the as-grown and transferred graphene on r-plane sapphire substrate were determined by Raman spectroscopy (Horiba JY, LabRam HR 800) using an Ar<sup>+</sup> Laser (wavelength = 514 nm) as an exciting source. The X-ray photoelectron spectroscopy (XPS) measurement was studied by a high resolution XPS system (Thermo Fisher, ESCALAB 250xi) using Al ( $K\alpha_1$ , 1486.6 eV) as an excitation source. The structural damages of the annealed samples were investigated by digital microscope (Leica, DM4000 M) and high resolution field-emission scanning electron microscope (SEM) (JEOL, JSM-6700F) with a voltage of 5KV. The electrical properties of the as-transferred and annealed samples were carried out by a non-contact Hall system (LEI, LEI 1610) using microwave probing at room temperature.

## 3. Results and discussion

### 3.1. Surface morphology analysis by AFM, optical microscopy and high-resolution SEM

Fig. 1 shows the optical microscopy images of the annealed graphene/r-sapphire samples in an objective lens magnification of 50 $\times$ . These pictures gave us a panoramic view of the morphological variation with the thermal process. It illuminated that the as-transferred sample had a perfect surface uniformity with little visible defects in the area of sight (500  $\times$  500  $\mu\text{m}^2$ ). A considerable amount of polymeric residues (marked by white circles) on the surface of the as-transferred sample (Fig. 1a) had no other structural defects. As seen in Fig. 1b–f, when the temperature of thermal annealing rises, the amount of polymeric residues and their particles size notably decreased; by contrast, the filament or flocculus (white squares) increased. These phenomena have not been mentioned in the previous efforts on the thermal annealing process. Thus, it was necessary to figure out what the filament or flocculus is, as well as its forming mechanism.

In order to get a further analysis of the morphological alteration during the annealing, especially the filament or

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