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Research paper

Effects of chemical and physical defects on the humidity sensitivity of graphene surface

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ABSTRACT

We investigate the effect of the chemical and physical defects on the humidity sensitivity of graphene. For this we apply reactive ion etching for physical defects and the poly(methyl methacrylate) (PMMA) coating for chemical defects to the CVD graphene. The tendency of humidity sensing is hardly found by the physical defects while the distinct changes are observed with chemical defects by control of the thickness and the coverage area of the PMMA on the graphene surface. The graphenes covered with thinner or smaller area of PMMA show an enhanced humidity sensitivity, indicating the possibility of H_2O sensing.

1. Introduction

As one of the crystalline carbon structures, graphene is well known for its various kinds of applications [1–4]. Among them, one of the representative applications is the gas sensors. Electrical properties graphene are effected by a few molecules adsorbed on the surface of graphene. [5]. Among them, H_2O molecules can be readily doped on graphene surfaces [6,7], implying that graphene could be used as a promising material in humidity sensing applications, but, it is still challenging to achieve high sensitivity for water molecule. In some reports, graphene derivatives like graphene oxide (GO) and reduced graphene oxide (rGO) had been chosen for the sensing material for humidity change [8,9]. GO and rGO are hydrophilic due to oxygen functional groups [10,11], so it is possible to obtain high humidity sensitivity. However, the structure of the GO layer on the substrate, is layer by layer structure of GO flakes [8,9], so it is hard to apply photolithography process and GO itself can have degradation in humid air because of its high solubility in water.

The graphene grown by chemical vapor deposition (CVD) is favored in most of the graphene devices, because it is easy to obtain the mono layer of graphene in a large scale [12,13], so it is useful to apply mass production. There are already some reports about the humidity sensor using CVD graphene [14,15]. Despite these advantages of the CVD graphene, there are some factors to carefully consider when we fabricate the humidity sensor using graphene. The first thing is the polymer residue on the graphene. Wet transfer method are a frequently used method for transferring the CVD graphene [4,12,16], but after transferring graphene by the this method, the PMMA residues remain on the surface of graphene [16]. However, completely removing the polymer residues is impossible [16], and not only the PMMA residues have a doping effect for the graphene [17], but also PMMA residues on the graphene can adsorb water molecules [18,19] so that the electrical properties of graphene can be effected. The second thing is that the CVD graphene intrinsically have various kinds of defects on it [20,21]. The defects on the graphene effects the adsorption of several gas molecules including water molecules [20,22–26]. Therefore, it is necessary to consider the amount of PMMA residues and defects the on the graphene when making the humidity sensor using graphene or the graphene devices under humidity changing conditions.

In this study, we report the effect of the physical and chemical defects on the CVD graphene for humidity sensing. The physical defects on the graphene were created by reactive ion etching (RIE). To tailor the chemical defects on the graphene, we covered the PMMA on the graphene surface with different coverage areas and thicknesses using spin coating. To examine the humidity sensitivity, the resistance changes of the modified graphene were measured under the various humidity environment. Effects of the physical and chemical defects were demonstrated in terms of the enhancement of the humidity sensitivity of the graphene.

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2. Experimental section

To study the effect of physical defects on humidity sensitivity of graphene, defects in the graphene samples were controlled using a plasma etching process. The fabrication process of the graphene having defects is depicted in Fig. 1(a). CVD graphene was transferred onto a SiO_2/Si substrate by a wet transfer method and a Cr/Au electrode (5 nm/30 nm thick) was deposited using an E-beam evaporator. The size of the graphene sample exposed to air was 7 mm × 10 mm. Subsequently, the graphene sample was etched with oxygen plasma at 20 W and an O_2 gas flow of 20 standard cubic centimeters per minute (sccm) at 110 mTorr. The etching time of the samples was varied as 0, 1, 2, and 4 s for inducing defects on the graphene samples [27]. The graphene almost destroyed with further etching time over 4 s, so we didn't tested. For a convenience, we call the graphene sample with 0 s etching time as the pristine graphene. The sample was then placed in a quartz tube and the electrodes were connected to a multimeter (Keithley 2002) for measuring the sample resistances. All the experiments were performed at room temperature. Through the tube inlet, air with 4% or 72% relative humidity (RH) was flown into the tube. The humidity was controlled using a mass flow controller and a bubbler. Initially, dry air (4% RH) was flown into the tube with a rate of 500 sccm for 1 h in order to stabilize the resistance of the sample. Then, humid air (72% RH) was passed at a rate of 500 sccm into the tube for 300 s followed by passing dry air at a rate of 500 sccm for 300 s. We repeated the airflow with different RH values 7 times, each with a duration of 300 s, and we repeated this humidity test for 3 times with the same samples.

The resistance of the sample at time t is denoted as R(t). The initial resistance obtained in dry air after the first cycle is denoted as R_0. The change in the resistance can be obtained as follows:

$$\frac{\Delta R}{R_0} = \frac{(R(t) - R_0)}{R_0}$$

For convenience, the humidity sensitivity is defined as the average value of the resistance changes measured in 6 cycles under humid air and dry air conditions.

To verify the effects of PMMA on the graphene samples, graphene was coated with PMMA layers of different thicknesses and coverage areas. The fabrication processes are shown in Fig. 1. After depositing the electrodes and connecting copper wire on the electrodes, we coated the PMMA layer on the graphene. To vary the thickness of the PMMA layer, we diluted the PMMA solution (MicroChem, 950 k, C4) with mono chlorobenzene, and coated the diluted solution on the graphene by spin coating. The concentrations of PMMA solutions we obtained were 0.5 wt%, 1 wt%, 2 wt %, and 4 wt% (not diluted). The condition of the spin coating was at 3000 rpm for 30 s. The samples coated with PMMA were heated on a hot plate at 180 °C for 1 min in order to cure PMMA on the

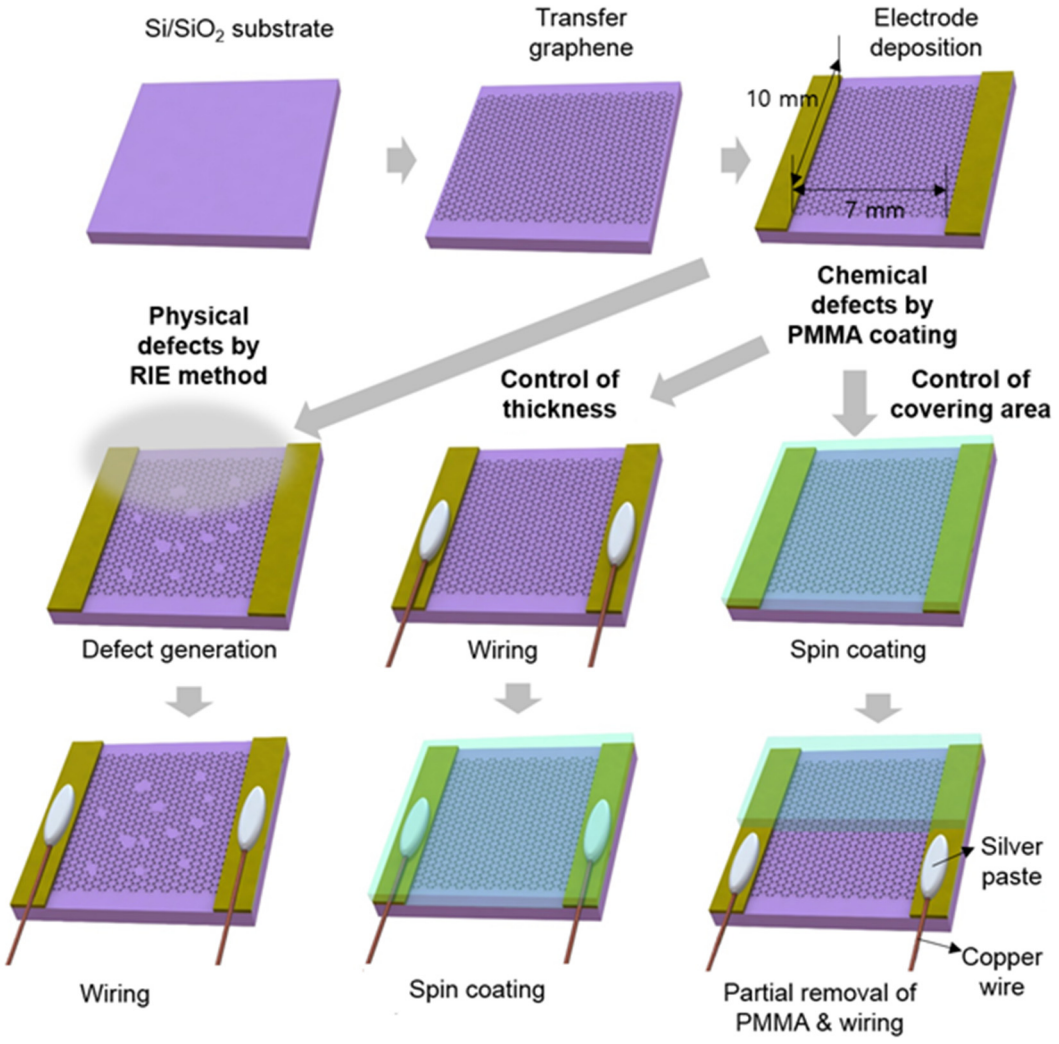

Fig. 1. Fabrication process of modified CVD graphene with RIE method, PMMA treatment (thickness and coverage area variation).