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Abstract. Graphene shows promise for applications in flexible electronics. Here, we describe our procedure to transfer graphene grown on copper substrates by chemical vapor deposition to polydimethylsiloxane (PDMS) and SiO_2/Si surfaces. The transfer of graphene was achieved by a simple, etching-free method onto flexible PDMS substrates.

1. Introduction

Graphene is a single layer of carbon atoms arranged in a honeycomb lattice, and since its first isolation in 2004, the material has attracted tremendous attention due to its novel properties and potential applications [1–3]. In particular, graphene is promising for flexible electronics due to its high optical transparency, physical flexibility, and electrical conductivity [4–6]. Recent developments in the chemical vapor deposition (CVD) method have enabled the successful production of large scale, single layers of graphene (SLG) or few layer graphene (FLG) on metal catalytic surfaces such as Cu, Ni, Pd, Ru or Pt [7–10]. However, for practical flexible-electronic applications, graphene must be transferred to appropriate substrates such as polystyrene (PS), polyvinyl alcohol (PVA), polymethylmetacrylate (PMMA), and polydimethylsiloxane (PDMS) [11–14]. Here, we describe our procedure to transfer graphene deposited on copper (Cu) substrates to PDMS and SiO_2/Si surfaces by chemical etching methods. Furthermore, we also describe the results of experiments on transfer based on an etching-free procedure, where the graphene was transferred by a facile peel-off process for easily exfoliating graphene from Cu surfaces onto flexible surfaces of PDMS substrates. Notably, we demonstrate that the transferred graphene on PDMS by etching-free, not only no significant Raman shift, but also higher 2D/G peak ratio compared to that transferred etching method on the PDMS surface. Optimization for synthesis of the graphene was growth at 1000 °C for 15 min, with growth pressure of 5 Torr, C_2H_2 gas flow rate of 20 sccm and Ar gas flow rate 500 sccm. Furthermore, our approach can be renewable metal substrates, chemical-free, environment-friendly and economy of time. Finally, Transferred graphene on the flexible surface of PDMS can be possible of application in many electronic devices, such as flexible thin-film, solar cells, and touch panels.

2. Experimental

We used chemical vapor deposition (CVD) for the deposition of graphene onto Cu foils using C_2H_2/Ar (20 sccm : 500 sccm), at 5.0 Torr reactor pressure, substrate temperature of 1000 °C followed by rapid cooling to room temperature. The PDMS pre-polymer was prepared by mixing a silicone elastomer base with a curing agent with a ratio of 10:1. The PDMS and curing agent (Silpot 184 and Catalyst Silpot 184) were purchased from Dow Corning, Toray Co., Ltd. A solution of TBAF (tetrabutylammonium fluoride) in NMP (N-Methelpyrrolidone) (5:1; v/v; NMP/75% TBAF in water, TCI, Tokyo, Japan) was used to sufficiently dissolve the PDMS without leaving a residue at room temperature for 24 hours. All the Raman spectra were measured by a Nihon Bunko NRS-7100 system with excitation light of a 532 nm laser, with an estimated laser spot of less 1 μm.

3. Results and Discussion

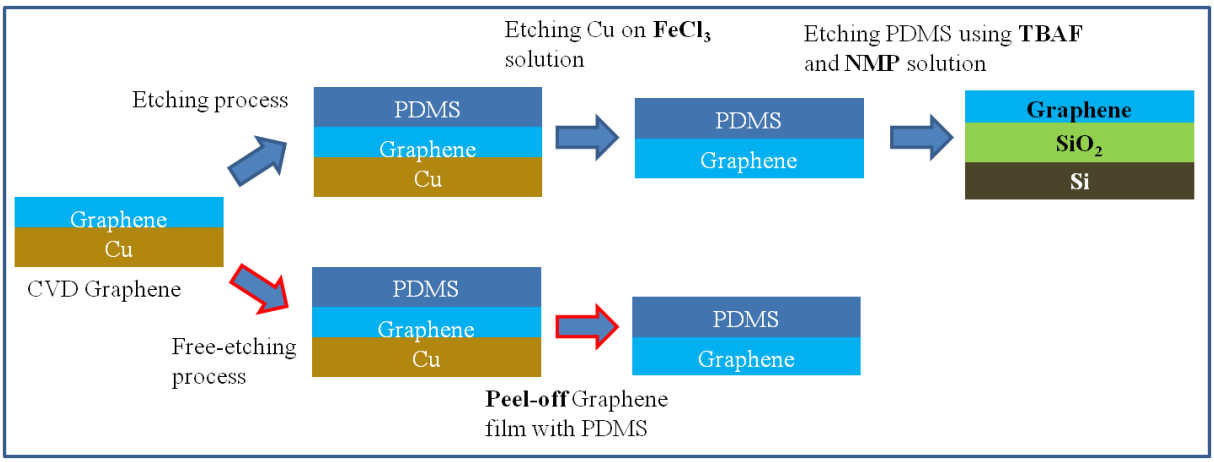

Figure 1. Schematic diagram of the processes used for transferring graphene from copper foils to target substrates using etching and etching-free methods.

Figure 1 is a schematic of the steps used to transfer graphene from copper foil substrates to flexible PDMS substrates using $FeCl_3$ etching and the etching-free, direct peel-off method. We deposited graphene on copper foils by CVD at 1000 °C in a gas mixture of C_2H_2 : Ar = 20 : 500 sccm. The liquid mixture of PDMS and curing agent (PDMS : curing agent = 10 : 1) was poured on the surface of the graphene-Cu foils. Next, the PDMS mixture was placed into a vacuum chamber for 30 min to remove bubbles. We prepared same substrate of graphene-Cu on solid PDMS for using chemical-etching and etching-free experiments.

In the chemical etching process the Cu foil was etched using $FeCl_3$ for 24 h and the graphene transferred using PDMS. The PDMS-graphene was attached onto a SiO_2/Si substrate and the PDMS dissolved in a solution of TBAF : NMP (mixing ratio of 10 : 1) at room temperature for 24 hours.

In the etching-free process, a solid layer of PDMS was slowly removed from the Cu substrate. This resulted in the graphene being transferred to the PDMS surface because the

adhesion force of PDMS-graphene is higher than that between the graphene-graphene. We noticed that the ratio of the PDMS and curing agent determined the adhesion force between PDMS and target substrate.

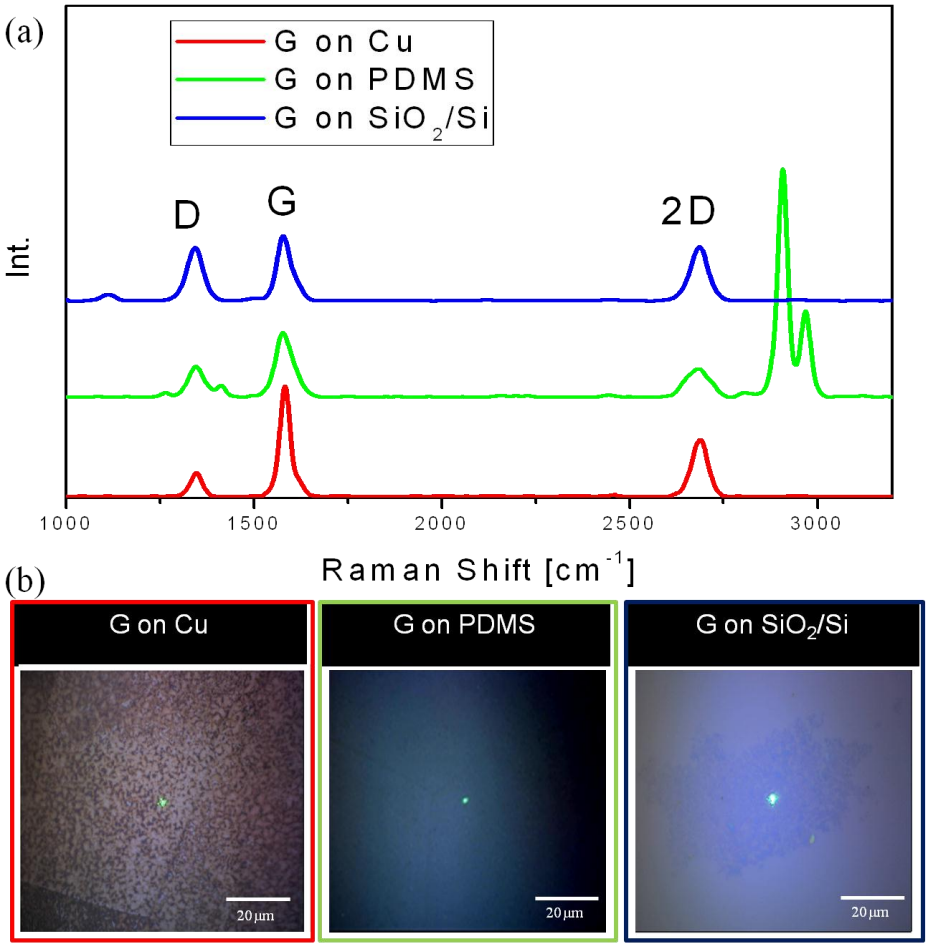

Figure 2. (a) Raman spectra and (b) optical microscope images show graphene on Cu, PDMS, and SiO_2/Si substrates.

Figure 2 (a) shows Raman spectra of graphene on Cu, PDMS, and SiO_2/Si substrates. Few-layered graphene resulted by CVD growth at 1000 °C (C_2H_2 : Ar = 20 : 500 sccm). The sharp peaks of graphene-Cu spectrum are due to graphene with the three signature peaks at 1345 cm^{-1} (D peak), 1576 cm^{-1} (G peak), and 2681 cm^{-1} (2D peak). The PDMS graphene was

transferred from the CVD graphene-Cu by etching Cu with $FeCl_3$ solution. The graphene transferred to PDMS showed D, G, and 2D peaks and no significant changes. However, the Raman spectra showed an increase of the intensity of G to D peak (I_G/I_D) after chemical etching with $FeCl_3$, indicating the possibility of damage of the graphene surface layer [15]. Furthermore, the intensity of (I_G/I_D) of the graphene transferred to SiO_2/Si by dissolving in a solution of TBAF/NMP increased. Figure 2(b) shows optical microscopic images of graphene on Cu, PDMS, and SiO_2/Si substrates.

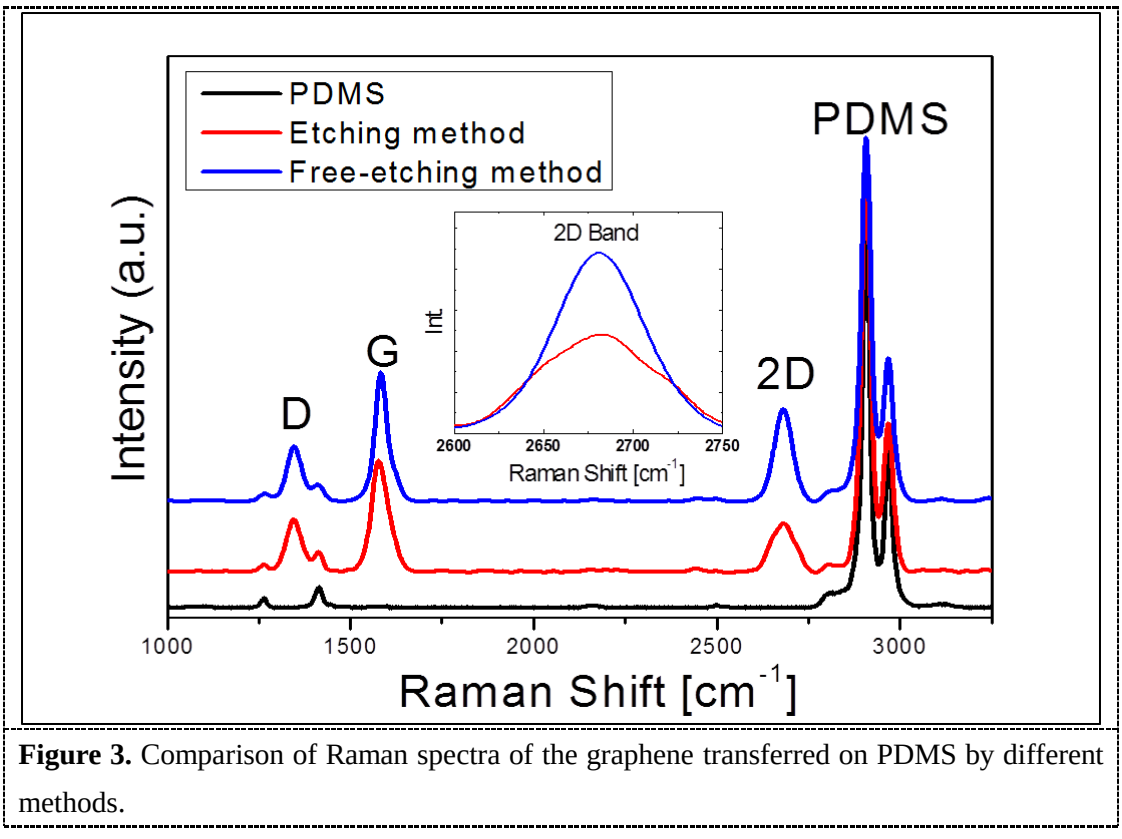

Figure 3. Comparison of Raman spectra of the graphene transferred on PDMS by different methods.

Figure 3 is a comparison of Raman spectra of graphene transferred onto PDMS by etching copper, etching-free, and PDMS based methods. The PDMS (black line) peaks were observed for all transferred samples by etching PDMS (red line) and free-etching PDMS (blue line). The D 1345 $cm^{-1}$and G 1576 cm^{-1} band positions and values of the G-to-D peak ratio (I_G/I_D)

were similar for etching (~ 2.06) and etching-free (~2.15) samples. However, the full width at half maximum (FWHM) of the 2D Raman band of the etching-free sample was narrower than the etching sample, with the etching sample being 80.4 cm^{-1} and etching-free 55.9 cm^{-1}, respectively. The shape, 2D to G peak ratio (I_{2D}/I_G), and FWHM of the 2D band was used to determine the number of graphene layers because the 2D band originates from the two phonon double resonance process and is closely related to the band structure of graphene layers [16]. Therefore, the narrow 2D peaks imply that the etching-free method can transfer few-layered graphene.

4. Conclusion

We described two simple methods etching and etching-free for transferring graphene grown on Cu substrates onto flexible surfaces of PDMS and silicon. We successfully transferred graphene onto flexible surfaces from Cu substrates without chemical etching. Chemical etching with $FeCl_3$ led to an increase in the (I_G/I_D) ratio indicating the formation of chemical induced damage in the graphene layer. The observation of a narrow 2D peak from graphene transferred by a etching-free implied the possibility of transferring few-layered graphene onto flexible surfaces. The graphene on flexible PDMS opens up the possibility of applications for electronic devices such as solar cells and touch panels.

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