Study of the Electronic Properties and Strain sensitivity of Chemical Vapor Deposition-Grown Graphene from C_2H_2

Meng Yang, Shinichiro Sasaki, Masato Ohnishi, Ken Suzuki and Hideo Miura

Fracture and Reliability Research Institute, Graduate School of Engineering, Tohoku University
6-6-11-716, Aoba, Aramaki, Aobaku, Sendai Miyagi 980-8579, Japan
Phone: +81-22-795-4830 E-mail: youmou@rift.mech.tohoku.ac.jp

Abstract

We succeed in synthesizing large-area single layer graphene using low pressure chemical vapor deposition (LPCVD) process from C_2H_2 gas. The CVD growth exhibits self-limiting behavior. A carrier mobility of ~1150 cm^2/Vs and a gauge factor 3.4 for were achieved by measuring the fabricated graphene FETs and strain sensor, revealing the potential for large-scale FETs and strain sensors applications.

1. Introduction

Graphene has exhibited great potential for electronic applications due to its high mechanical strength, superior electronic properties and good compatibility with the traditional semiconductor process. From an application point of view, large-area, uniform monolayer graphene films with low defects are required. Chemical vapor deposition (CVD) using CH_4 precursor is the most common synthesis method, which can control the layer number and nucleation density of graphene more easily than C_2H_4 and C_2H_2. In addition, in order to form uniform single-layer graphene sheets, generally highly diluted CH_4 gas is indispensable for the low pressure CVD (LPCVD) and atmospheric pressure CVD (APCVD) process, leading to the long growth time. The long growth time should consume large amounts of energy an increase the production cost.

C_2H_2 has ever been used for the CVD synthesis of multilayer graphene on both Cu and Ni substrates. Due to its low dissociation bond energy, C_2H_2 should be a promising carbon source to from graphene at high growth rate and low temperature. On the other hand, because of the high reactivity and large amounts of carbon supply from C_2H_2, a dense nucleation of multi-layer graphene grains with amorphous structure is highly preferred. Thus, it is difficult to observe the nucleation process and form single-layer graphene with high quality by LPCVD and APCVD process. To date, single-layer graphene with large area can only be formed using the ultrahigh vacuum CVD (UHVCVD) process at extremely low partial pressure [1]. However, this process require long growth time (>1 h) and high equipment cost. In this study, we succeed in growing single layer graphene using LPCVD process. By fabricating graphene-based field effect transistors (FETs) and flexible graphene-on-polydimethysiloxane (PDMS) strain sensors, the electronic properties and strain sensitivity of our C_2H_2 CVD-grown graphene are investigated, respectively.

2. Self-limiting Growth of Graphene from C_2H_2

Graphene was synthesized using thermal CVD apparatus (ULVAC QH-P610CP) with a quartz tube. Cu foils (Nilaco CU-113263, 50μm-thick, 99.9%) served as the catalyst. In order to remove the impurities, the Cu foils were dipped into a nitric acid solution (5 wt %) for 60s and then cleaned using an ultrasonic cleaner for 10 min in acetone and ethanol to eliminate the organic impurities. Then the Cu foils were folded into pockets and heated on the hot plate in air for 90 min at 250℃ (Fig. 1(a)) [2]. We found that the Cu pockets and peroxidation process can significantly suppress the nucleation density and the formation of multilayer graphene. The synthesis process by our LPCVD is described in Fig. 1(b). The copper pockets were heated to 1035℃ in vacuum and then annealed for 40 min under the constant flowing rate of 14 sccm H_2. The pressure was kept at 2.4 torr in the annealing process. Then C_2H_2 and H_2 gas
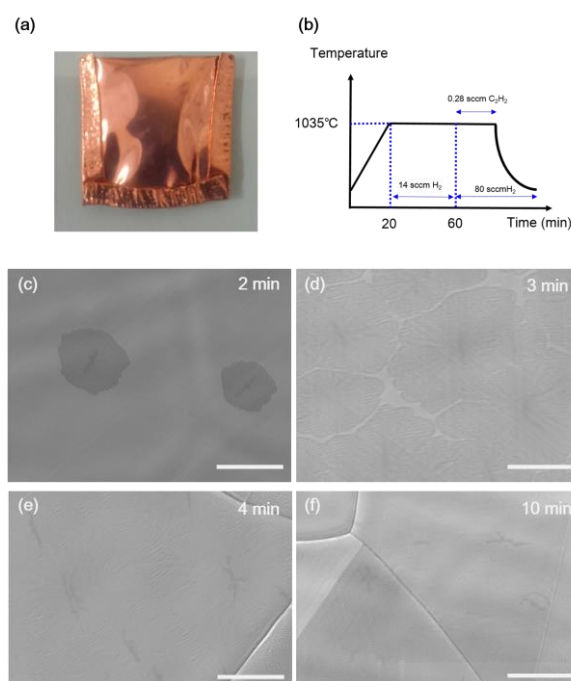

Fig. 1 (a) Photograph of the copper pockets used for CVD growth. (b) Experimental diagram for growth of graphene including ramping, annealing, growth and cooling process. (c-f) SEM images of as-grown graphene on the inner surface of the Cu pockets with different growth duration. All scale bars are 20 μm.

with the flow rate of 0.28 and 80 sccm were imported into the quartz to grow graphene with a total pressure of 0.8 torr. After CVD growth, the samples were cooled down to room temperature under the same H_2 atmosphere but without C_2H_2 supply. SEM images of as-grown graphene on the copper surface with different growth duration are shown in Fig. 1(c)-(f). Graphene grains nucleate on the inner surface of the Cu pockets. With the increase in the growth duration, these graphene grains grow and coalescence with each other. After 4 min, continuous graphene sheet was formed and an extended growth time resulted in no further growth, revealing the self-limiting growth of graphene.

3. Structural Characterization by Raman Spectroscopy

The as-grown graphene was transferred onto a SiO_2/Si substrate based on the wet transfer process. 2 wt% poly(methyl methacrylate) (PMMA) resist (Microchem PMMA 950K A2, 2% in anisole) was coated onto the sample, followed by etching the Cu layer with $FeCl_3$ solution After the PMMA/graphene film was transferred onto the 300 nm SiO_2/Si substrate the PMMA resist was removed by acetone (Fig. 2(a)). The carbon bonding state of the transferred graphene is evaluated using Raman spectroscopy (Jasco NRS-5100). As shown in Fig. 2(b), the typical G band at 1580 cm^{-1}, and a 2D band at 2700 cm^{-1} can be observed with an intensity ratio (I_{2D}/I_G) larger than 1.8. In addition, the symmetric 2D band with a full width at half maximum (FWHM) less than 35 cm^{-1} can be observed, revealing that our graphene is single layer [3]. No significant difference in Raman spectrum can be observed for graphene after the CVD growth for 4 min and 10 min, indicating the self-limiting growth of single-layer graphene. The small D band at 1350 cm^{-1} indicate the low defect of our C_2H_2-grown graphene. By mapping the I_{2D}/I_G intensity ratio and the FWHM for an area as large as 30 μm×30 μm, we found that nearly 95% is single-layer graphene.

4. Electronic Property and Strain Sensitivity of Single-layer Gaphene from C_2H_2
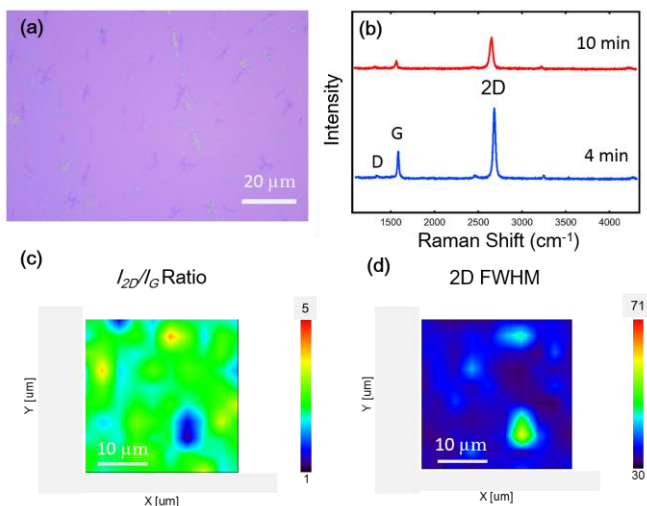

Fig. 2 (a) Optical image of graphene transferred onto SiO_2/Si substrate. (b) Raman spectroscopy of graphene with the growth duration 4 min (blue) and 10 min (red). Raman mapping for the I_{2D}/I_G ratio (c) and 2D FWHM (d) of graphene transferred onto SiO_2/Si substrate.

To characterize the electronic properties of graphene, as shown in Fig. 3(a), back-gate graphene field-effect transistors (FETs) were fabricated. The graphene layers transferred onto SiO_2/Si substrate were contacted with Pt/Au electrodes deposited by electron beam metal vapor deposition through a photolithography process (Fig. 3(a)). The graphene FETs were loaded into a probe station and measured with a semiconductor parameter analyzer (Agilent 4155C) at room temperature under atmosphere environment. As shown in Fig. 3(c), grapheen FETs exhibit clear ambipolar charcateristics. The measured sheet resistance and extracted carrier mobility is ~1130Ω/sq and ~1150 cm^2/Vs, which is comparable to that of graphene grown from CH_4. We also fabricated graphene-based strain sensor on as-grown graphene/Cu substrates by photolithography process and transfer the device onto a polydimethysiloxane (PDMS) substrate. A motorized stage (Chuoseiki ALS-305-CM) is used to perform the tensile test as shown in Fig. 3(b). The strain sensor can sustain a large deformation up to 8%, and the extracted gauge factor is 3.4 (Fig. 3(d)).

5. Conclusions

Single-layer graphene was formed by LPCVD process using C_2H_2 gas as the carbon source. Our single-layer graphene exhibits high quality comparable to that of grapahene grown from CH_4. We investigated the electronic properties and the strain sensitivities of our CVD-grown graphene, revealing that our graphene has the potential for large-scale FETs and strain sensors applications.

Acknowledgements

References

[1] N. S. Mueller *et al*., Carbon, 78 (2014), 347-55.
[2] X. S. Li *et al*., Journal of the American Chemical Society, 133 (2011), 2816-19.
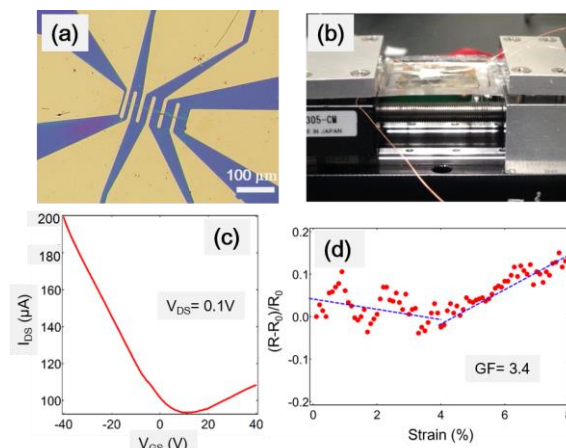[3] Graf, Davy, *et al.,* Nano letters 7.2 (2007), 238-242.

Fig. 3 (a) Optical image of graphene-based back-gate FETs. (b) Photograph of graphne strain sensors fixed in motorized stage bonded with Cu wires for electronic measurement. (c) I_{DS}-V_{GS} curve of FET device at V_{DS} =0.1 V. (d) Relative variation of the resistance of the graphene-based strain sensor under uniaxial tensile strain. Blue dot line is the fitted line to extract the gauge factor.