



# Growth characteristics of graphene synthesized via chemical vapor deposition using carbon tetrabromide precursor



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## ABSTRACT

A carbon tetrabromide (CBr<sub>4</sub>) precursor was employed for the chemical vapor deposition (CVD) of graphene, and the graphene growth characteristics as functions of the following key factors were then investigated: growth time, growth temperature, and the partial pressure of the precursor. The graphene was transferred onto a SiO<sub>2</sub>/Si substrate and characterized using transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy, and the electrical properties were measured through the fabrication of field-effect transistors. Our results show that high yield and controllable growth are possible via CVD used with a CBr<sub>4</sub> precursor. Thus, CBr<sub>4</sub> precursor is a new alternative candidate for use in the mass production of graphene.

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## 1. Introduction

Graphene, a two dimensional sp<sup>2</sup> hybridized carbon material, has attracted considerable attention because of its remarkable electrical, optical, chemical, and mechanical properties. These properties include extremely high carrier mobility [1–3], high optical transparency [4], chemical stability, and high elasticity [5]. In recent years, catalyst-assisted thermal chemical vapor deposition (CVD) using a methane (CH<sub>4</sub>) precursor and a pure Cu foil has been widely used for large-scale and high-quality graphene growth. This is because of the self-limiting process at low pressure caused by the low solubility of carbon in Cu [6–11]. However, graphene CVD using CH<sub>4</sub> on Cu foil (CH<sub>4</sub>-graphene) requires a high growth temperature (*T<sub>s</sub>*) of over 900 °C and produces graphene with limited yield, which is inappropriate for the mass production of this material. While microwave plasma CVD using CH<sub>4</sub> on Cu foils has been applied to successfully stimulate the rapid growth of few-layer graphene over a 100 s period, the experimental setup is complex and no significant reduction in graphene film thickness has been shown [12].

The high *T<sub>s</sub>* of CH<sub>4</sub>-graphene is attributed to its high energy barrier to dehydrogenation, which is related to the high bond

dissociation energy of C–H (approximately 105 kcal·mol<sup>-1</sup> at room temperature) in CH<sub>4</sub> [13]. Graphene growth using other aliphatic hydrocarbon precursors also requires high *T<sub>s</sub>*, again owing to the high bond dissociation energy of C–H (approximately 131 kcal·mol<sup>-1</sup> for C<sub>2</sub>H<sub>2</sub>, 110 kcal·mol<sup>-1</sup> for C<sub>2</sub>H<sub>4</sub>, and 98–100 kcal·mol<sup>-1</sup> for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>) [11,14–16]. On the contrary, carbon tetrabromide (CBr<sub>4</sub>) has a bond dissociation energy equal that of C–Br (approximately 56 kcal·mol<sup>-1</sup>) [17,18], which is lower than those of other halocarbon precursors (approximately 124 kcal·mol<sup>-1</sup> for C–F in CF<sub>4</sub> and 71 kcal·mol<sup>-1</sup> for C–Cl in CCl<sub>4</sub>) [19] and those of the aliphatic hydrocarbon precursors mentioned above. Furthermore, CBr<sub>4</sub> precursor forms reactive radicals at approximately 300 °C and reaches a sufficient vapor pressure of 1 Torr at 60 °C [20].

However, low bond dissociation energy is neither a necessary nor sufficient condition for low-temperature graphene growth. Hence, the low-temperature growth of graphene was not the main focus of this study. Rather, this study focused on the growth characteristics of graphene with CBr<sub>4</sub> and compared the findings with the results of CH<sub>4</sub> graphene. Paddison et al. observed that CBr<sub>4</sub> is decomposed into successive bromomethyl radicals under hydrogen atmosphere [21]. These bromomethyl radicals are more reactive than CBr<sub>4</sub>, and they therefore evolve into more thermodynamically stable carbon species and form sp<sup>2</sup> honeycomb-chained graphene on the metal surface [22]. Hence, interesting

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results about the  $\text{CBr}_4$ -based CVD growth of graphene can be expected.

In this study, we examined graphene growth on Cu foil using CVD and employing  $\text{CBr}_4$  precursor and systematically varied the growth time ( $t_g$ ), the partial pressure of the  $\text{CBr}_4$  precursor ( $P_s$ ), and  $T_s$ . To the best of our knowledge, no studies have been published to date pertaining to the synthesis of graphene using  $\text{CBr}_4$  precursor as the carbon source. The CVD approach employing  $\text{CBr}_4$  precursor used in this study exhibits interesting experimental results, specifically, high yield and controllable graphene growth.

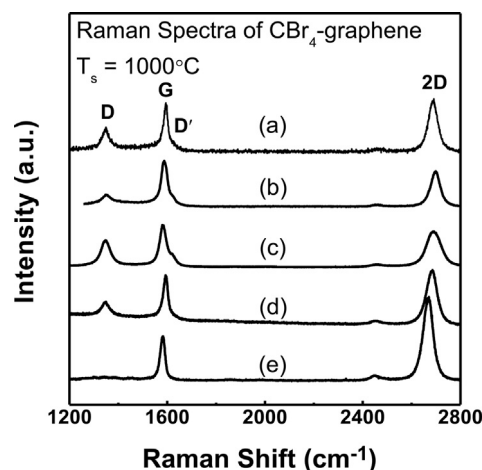
## 2. Experimental

The experimental chamber used for graphene growth via CVD consists of a quartz tube furnace pumped down to  $10^{-3}$  Torr, with the flow of hydrogen (99.9999%) and argon (99.999%) being controlled using mass flow controllers. Here, a pure copper foil ( $2 \times 2 \text{ cm}^2$ ) was cleaned in an ultrasonic bath using acetone, isopropyl alcohol (IPA), and deionized (DI) water. The Cu foil was then heated to  $1000^\circ\text{C}$  at a rate of  $30^\circ\text{Cmin}^{-1}$ , and annealed in an argon (600 sccm) and hydrogen (400 sccm) gas mixture flow for 30 min in order to reduce the native Cu oxide and to facilitate grain growth [23].  $\text{CBr}_4$  precursor (Sigma-Aldrich), vaporized in a canister at  $50^\circ\text{C}$ , was immediately introduced into the tube furnace along with an Ar (1000 sccm) and  $\text{H}_2$  (200 sccm) gas mixture (total chamber pressure of approximately 3.5 Torr).  $P_s$ , which was set to 1, 5, and 20 mTorr, was controlled by a needle valve and monitored using a digital vacuum gauge. The temperature dependence was investigated by adjusting  $T_s$  to 400, 500, 600, 700, 800, and  $1000^\circ\text{C}$ , and the time dependence was also studied by changing  $t_g$  between 8, 15, 60, and 120 s. To facilitate a comparative study of the growth yields of CVD-grown graphene using  $\text{CBr}_4$  precursor ( $\text{CBr}_4$ -graphene) and  $\text{CH}_4$ -graphene,  $\text{CH}_4$  precursor with a  $P_s$  of 20 mTorr was injected into the tube furnace during a growth step under the fixed  $\text{H}_2/\text{Ar}$  gas flow and at  $T_s$  values of 800 and  $1000^\circ\text{C}$ . The low temperature CVD below  $800^\circ\text{C}$  using  $\text{CH}_4$  was not tested because this condition does not satisfy the minimum requirement for thermal CVD of graphene. Also, this process was carefully carried out after the tube furnace was thoroughly cleaned.

A common transfer method was used to transfer the graphene films to the target substrates, as described below. A 4% solution of poly(methyl-methacrylate) (PMMA, Sigma-Aldrich) in anisole was first spin coated on the graphene/Cu foil and dried for 30 min at room temperature. Then, the graphene/PMMA film was released from the Cu foil by chemically etching the foil with ammonium persulfate (0.2 M) solution for 12 h, followed by rinsing with DI water. The floating PMMA-supported graphene was transferred onto a  $\text{SiO}_2$  (285 nm)/Si substrate, or lacey grid. Next, the sample was washed twice in a hot ( $50^\circ\text{C}$ ) acetone bath in order to remove the PMMA. The same procedure was used to transfer the CVD graphene to a heavily doped *p*-type silicon wafer with a 285-nm-thick  $\text{SiO}_2$  layer for device fabrication.

Scanning electron microscopy (SEM; JSM-6700F) was used to observe the morphology of the as-grown graphene and the graphene transferred onto the  $\text{SiO}_2/\text{Si}$  substrate. Raman spectroscopic measurements (Jobin Yvon ARAMIS, Ar-ion laser excitation wavelength: 532 nm, laser beam size:  $1 \mu\text{m}^2$ ) were conducted to investigate the optical properties of the graphene. High-resolution transmission electron microscopy (HRTEM; Tecnai F20, FEI) was used to measure the number of graphene layers, and X-ray photoelectron spectroscopy (XPS; Thermo VG, U.K., monochromated Al X-ray sources) was utilized for the chemical analysis of the  $\text{CBr}_4$ -graphene.

To fabricate back-gated graphene field effect transistors (BG-FETs), which were used to evaluate the electrical properties of



**Fig. 1.** Raman spectra of the transferred  $\text{CBr}_4$ -graphene film grown at  $T_s = 1000^\circ\text{C}$  for  $t_g =$  (a) 15 s, (b) 60 s, and (c) 120 s under  $P_s = 20$  mtorr, and for  $t_g = 120$  s under  $P_s =$  (d) 5 mtorr and (e) 1 mtorr.

the synthesized graphene, the  $\text{CBr}_4$ -graphene was transferred onto 285-nm-thick  $\text{SiO}_2$  on highly doped Si using the transfer technique mentioned above. Photolithography was used to thermally evaporate Ti (10 nm)/Au (50 nm) for source and drain electrodes on the transferred graphene films. Sequential  $\text{O}_2$  plasma etching was then used to create a graphene channel with a length ( $L$ ) of  $6 \mu\text{m}$  and width ( $W$ ) of  $4 \mu\text{m}$ . Four-probe electrical measurements were performed at ambient conditions. The gate voltage was applied through the back of the Si substrate, while the source-drain bias was constant at 0.1 V.

## 3. Results and discussion

As stated above, graphene growth on Cu foil was conducted through CVD employing  $\text{CBr}_4$  precursor, while  $t_g$ ,  $P_s$ , and  $T_s$  were varied systematically. The graphene films grown on Cu foil ( $T_s = 1000^\circ\text{C}$ ,  $P_s = 20$  mTorr) for  $t_g = 15$ , 60, and 120 s were transferred onto 285-nm-thick  $\text{SiO}_2$  substrates. The Raman spectra (Fig. 1) of these  $\text{CBr}_4$ -graphene films are found to have three primary peaks, D, G, and 2D, which are due to defects, the doubly degenerate zone center  $E_{2g}$  mode, and second-order zone-boundary phonons, respectively [24]. We measured the G to 2D and D to G peak intensity ratios in order to characterize the  $\text{CBr}_4$ -graphene. Note that these ratios are denoted in the literature as  $I(G)/I(2D)$  and  $I(D)/I(G)$ , respectively. We summarized the properties of  $\text{CBr}_4$ -graphene and the variable growth conditions as shown in Table 1. Each of those graphene samples is allotted a letter of the alphabet (from “sample a” to “sample e”), respectively. The  $I(G)/I(2D)$  value and full-width half maximum (FWHM) of the 2D peak (sample c;  $t_g = 2$  min) are approximately 1.25 and  $74 \text{ cm}^{-1}$ , respectively. These values indicate that multilayer graphene (MLG) is grown on the Cu foils [25,26]. To obtain thinner graphene films,  $t_g$  was decreased to 1 min. The Raman spectrum of the resultant  $\text{CBr}_4$ -graphene (sample b;  $t_g = 1$  min) shows that the  $I(G)/I(2D)$  value is approximately 1.18 and the FWHM of the 2D peak is approximately  $49 \text{ cm}^{-1}$ , indicating the formation of thinner graphene films. For a shorter growth period, the  $I(G)/I(2D)$  value of the  $\text{CBr}_4$ -graphene (sample a;  $t_g = 15$  s) is approximately 0.85 and the FWHM of the 2D peak is approximately  $45 \text{ cm}^{-1}$ , indicating few-layer graphene (FLG) formation. It is known that CVD FLG has an asymmetric 2D peak with FWHM values of  $45\text{--}54 \text{ cm}^{-1}$  [11]. In this study, as  $P_s$  drops to 5 mTorr (sample d), the 2D peak exhibits a FWHM of approximately  $54 \text{ cm}^{-1}$  and an  $I(G)/I(2D)$  value of approximately 0.85, which is indicative of FLG. As  $P_s$  is further decreased to

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