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Low Temperature Plasma CVD Grown Graphene by Microwave Surface-Wave Plasma CVD Using Camphor Precursor

Hideo Uchida[1], Hare Ram Aryal[1, 2], Sudip Adhikari[1, 2] and Masayoshi Umeno[2]

1. Department of Electronics and Information Engineering, Chubu University, Matsumoto 1200 Kasugai, Aichi 487-5801, Japan

2. Institute for General Research of Science, Chubu University, Matsumoto 1200 Kasugai, Aichi 487-5801, Japan

Abstract: Hydrocarbon precursor such as methane has been widely used to grow graphene films and the methods of growing quality graphene films are dominated by thermal CVD (chemical vapor deposition) system. Graphene films grown by plasma process are generally highly defective which in turns degrade the quality of the films. Here, using a green precursor, camphor we demonstrate a simple and economical method to get high-quality graphene film on copper substrate by micro wave surface-wave plasma CVD at relatively low temperature 550℃. Graphene film grown using camphor shows superior quality than that of the film grown using methane. Results revealed that camphor precursor is a good alternative to hydrocarbon precursors for graphene research.

Key words: Camphor, plasma CVD, quality graphene, plasma induced defects.

1. Introduction

Current approaches of growing high quality graphene films on Cu (copper) substrates are dominated by thermal CVD (chemical vapor deposition) system [1-3]. However, this method requires high temperature, around 1,000 ℃ in order to dehydrogenation of carbon precursors on Cu. High processing temperature restricts the possibility of improving compatibilities of the film with modern electronics technology. Moreover, the electrical properties of the films could be affected by thermally derived strain and topological defects [4].

Plasma CVD process could be a very good alternative of thermal CVD for growing graphene as the creation of plasma of the reacting gaseous precursors allows deposition at lower temperature with respect to thermal CVD. However, the quality of plasma-grown graphene [5, 6] has not been significantly better than that of thermal CVD. We believe that in addition of grain size, the origins of defects on the plasma deposited graphene films are the effects of ion bombardments and the effect of ultra violet radiation generated during plasma processing. Since plasma can damage the growing material, one needs to design the equipment in order to avoid the damaging effects of the plasma. Some approaches to graphene synthesis using MW (microwave) plasma CVD [7, 8] and SW (surface wave) assisted MW plasma CVD [5, 9] have been reported so far. However, the reports show very intensive D peak signals which ultimately lead to the poor quality film for its device applications.

Moreover, selection of the carbon precursor may also play vital role during graphene growth process. For instance, role of oxygen which already present in camphor molecule ($C_{10}H_{16}O$) may be very crucial to reduce nucleation density of graphene by passivating the Cu substrate. Hao et al. [1] discussed the role of surface oxygen in thermal CVD and showed that oxygen on Cu surface not only suppresses graphene nucleation, fostering growth of ultra-large graphene domains, but also lowers the carbon species edge

Corresponding author: Hideo Uchida, Ph.D., professor, research field: carbon materials and applications.

attachment barrier. This suggests that constituted oxygen in carbon source material, camphor could be very beneficial in order to get quality graphene film. Our results in this work also suggest that camphor is a very good alternative precursor to grow quality graphene not only because of constituted oxygen but also because that it is such a very cheap and green precursor that can be available abundantly in nature.

Here, we demonstrate a simple and economical method, avoiding direct exposure of the sample to the plasma to get high-quality graphene film on Cu substrate by micro wave surface-wave plasma CVD at relatively low temperature 550℃. The main aim of this work is to get low defective graphene films by using camphor precursor and compare the results with the film deposited by using methane precursor under identical experimental conditions.

2. Materials and Methods

Fig. 1 shows schematic representation of the MW SWP CVD system used in this research. MW SWP CVD is one of the most promising plasma sources which satisfy the requirements for large-area plasma processing tools. The advantage of SWP is that the high density plasma can be produced even at low pressure and Large–area uniform plasma can be produced using a slot antenna technique. Previously, we have reported this technique for the synthesis of amorphous carbon nitride thin films [10] and large area graphene film [5] at low temperatures. Detail of the growth technique is described elsewhere [10].

A green precursor, camphor was used as carbon source to grow graphene along with argon as a carrier gas. Graphene films were grown on pre-annealed Cu foils. Cu foils were annealed at 1,000℃ for 4 hours under 200 sccm (standard cubic centimeter per minute) H_2 flow using thermal CVD. The substrates were cooled down naturally to room temperature with a constant flow of H_2.

Pre-annealed substrates were placed inside the MW SWP CVD chamber, evacuated to 3×10^{-3} Pa and heated with constant flow of 100 sccm H_2 until the stage temperature reached up to 550 ℃. Camphor container and the pipelines were evacuated together with the main chamber of the CVD by turbo-molecular pump. Evacuation of the camphor container was performed carefully and early-staged camphor vapor was flushed out. Graphene growth were performed at 40 Pa gas composition pressure with the flow of 200 sccm argon and carbon precursor, camphor (98% purity, Wako chemical) vapor with the partial pressure of 2 Pa. Maintaining all

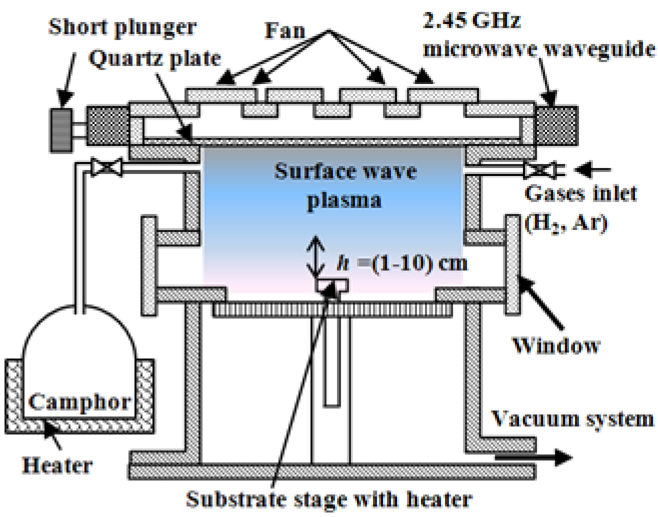


Fig. 1 Schematic representation of MW SWP CVD.

of the experimental conditions identical, successive growth experiments were performed by using methane precursor.

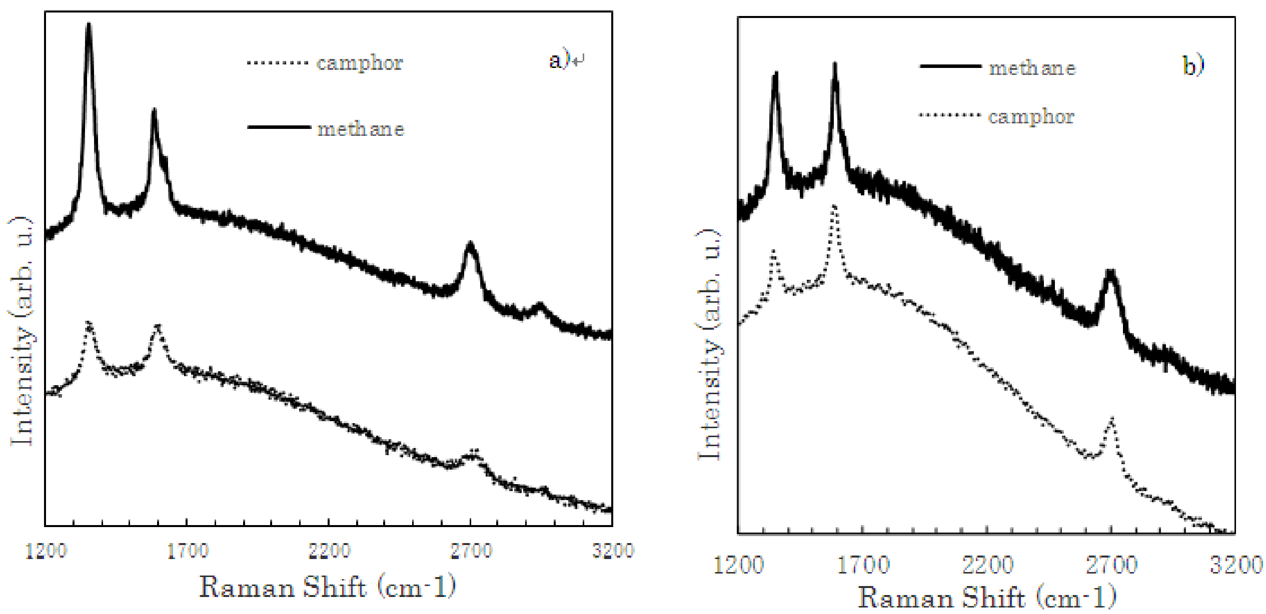
3. Results and Discussion

Graphene films deposited by this system generally show very intense defect peak while analyzing with Raman spectroscopy [5, 6]. We believe that in addition of grain size, the origins of defects on the plasma deposited graphene films are the effects of ion bombardments and the influence of ultra violet radiation generated during plasma processing. Since plasma can damage the growing material, one needs to design the equipment in order to avoid the damaging effects of the plasma. So, in order to reduce the plasma induced damages on the growing films, in this research, we deployed a very simple and economical method. A cover was placed above the substrate maintaining a height of 15 mm from substrate.

Fig. 2a shows typical Raman spectra signaled from as grown graphene film on Cu foil by using camphor and methane precursors. This is the case without placing a cover above the substrate. Strong signals of defect related peak, D peak centered at 1,346 cm^{-1} wave number is attributed to the plasma induced damages to the C-C sp^2 bonding which is suppressed by placing a cover and the related Raman spectra is presented in Fig. 2b. Other identifiable peaks are G peak at ~ 1,580 cm^{-1}, a radial C-C sp^2 bonded carbon stretching mode; and 2D peak at ~ 2,700 cm^{-1}, a second order zone boundary phonon mode.

The ratio of the intensity of D peak, I_D, to the G peak, I_G of the film deposited by direct exposure to plasma are 1.4 and 1.0 by using methane and camphor precursor, which are reduced to 0.9 and 0.6 respectively by placing a cover above the substrate during growth. This result clearly revealed the quality increment of the films by avoiding direct exposure of the substrate to the plasma. Moreover, the film deposited using camphor shows superior quality than that of the film deposited by using methane. Other defect related peaks such as D` peak around 1,625 cm^{-1} (shoulder peak of G peak) [5, 11] and the peak around 2,944 cm^{-1} is reduced preciously while placing cover above the substrate during growth.

These two defect-related peaks are almost invisible in the case of the film deposited by using camphor precursor, which indicates the merit of carbon source



(a) with direct exposure of substrate to plasma; (b) avoiding direct exposure of substrate to plasma.

Fig. 2 Raman spectra of as grown graphene on Cu foil:

Fig. 3 Schematic layout of sheet resistance and transmission measurement.

Table 1 Sheet resistance and transparency of graphene films grown by using camphor and methane precursor. The films were grown on Cu substrates by avoiding direct exposure of the plasma to the substrates.

Precursor	Sheet resistance (k-Ω/square)			Transmission (%) at 550 nm		
	Max.	Min	Average	Max.	Min.	Average
Camphor	6.47	3.26	4.71	95.16	91.45	93.35
Methane	7.96	4.52	5.26	93.63	88.20	91.30

material itself. We attribute this to the increase in the domain size of the graphene while using camphor precursor as the oxygen present in the camphor molecule may play a passivating role as suggested by Hao et. al [1].

Graphene films grown on Cu were transferred onto an arbitrary substrate, quartz by wet-etching of the underlying Cu in a Fe $(NO_3)_3$ solution with polymer support as described elsewhere [5].

Graphene films grown by using camphor and methane were separately transferred onto quartz substrates and their transparency and sheet resistance were measured. In order to check the uniformity of sheet resistance and transmission of the transferred graphene film on quartz surface the total area of 2 × 2 cm^2 graphene films were measured at nine points as shown in the schematic layout in Fig. 3.

Graphene films deposited by using methane precursor shows sheet resistance as low as 4.52 k-Ω/square with transmission as high as 93.63% at 550 nm wavelength. Resistance varies from 4.52 to 7.96 k-Ω/square whereas transmission percentage varies from 88.20 to 93.63. This result is better than previously reported reports by using same deposition techniques [5, 6]. This revealed the clear and straight forward advantageous impact of avoiding direct bombardment of plasma to the substrate. Average numbers of overall data measured at 9 different points are summarized in Table 1 along with minimum and maximum respective values.

Interestingly, graphene film deposited using camphor vapor shows superior qualities than that of the films synthesized using methane precursor. Graphene films deposited by using camphor precursor shows sheet resistance as low as 3.26 k-Ω/square and transmission as high as 95.16% at 550 nm wavelength. The resistance varies from 3.26 to 6.47 k-Ω/square whereas transmission percentage varies from 91.45 to 95.16. Average numbers of overall data measured at 9 different points are summarized in Table 1. We noticed that more transparent and less resistive film is achieved by using camphor. The results lead us to conclude that oxygen which is present in camphor molecule is beneficial not only to achieve larger domain size of graphene but also to reduce the thickness of the deposited film by etching carbon species during plasma processing.

4. Conclusion

Plasma induced damages on the graphene films are reduced by avoiding direct exposure of the substrate during growth. This was performed simply by placing a cover above the substrates. The influence of ion bombardment on the growing graphene film can be further reduced by lowering the cover height or allowing graphene growth onto the back-side of the substrates as suggest by Boyd et al. [11]. Present results show that camphor precursor could be the best choice for graphene growth at low temperature as oxygen present in the camphor molecule is seen to be beneficial for both controlling the thickness and passivating Cu substrate during growth.

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