Diamond & Related Materials 104 (2020) 107767

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Direct observation of graphene during Raman analysis and the effect of precursor solution parameter on the graphene structures

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ABSTRACT

Controlling the precursor solution parameter in preparing active catalyst film is critical in sol-gel process. The aim of this work is to validate the precursor solution parameter that affects the structural properties of graphene. Active Co_3O_4 film was prepared using precursor solution from cobalt acetate tetrahydrate in two different concentrations; 0.025 M and 0.05 M. One batch of the precursor solution was directly spin coated onto the substrate's surface meanwhile the second batch was kept for 4 days aging process. The studied spin speeds were 2000 rpm and 6000 rpm, and spin coated for 60 s. The active Co_3O_4 film was achieved by annealing at 450 °C and the graphene was grown at 900 °C of chemical vapor deposition (CVD) processing temperature for 5 min with the presence of ethanol as the carbon feedstock. The structural properties and morphology of the as-grown graphene synthesized from active Co_3O_4 film were characterized by Raman spectroscopy, optical microscope, and field emission scanning electron microscope (FESEM). The results demonstrated that concentration of precursor solution and the aging process affected the performance of the as-grown graphene. Agglomerates were formed in sample with 0.05 M of Co acetate tetrahydrate, however it was found that the Raman peaks intensity increased as compared to the 0.025 M sample. The precursor with 0.05 M has an acceptable chemical stability though aged for 4 days and contributed to the graphene growth. The spin coating speed was found not to affect the graphene growth at all. For aging effect, concentration 0.025 M shows unstable condition as compared to concentration 0.05 M when the precursor solution was aged for 4 days. Nonetheless, for the quality of the as-grown graphene, the ratio of Raman 2D-band over G-band intensities was less than 1.0, indicated that the graphene was in multi-layer form.

1. Introduction

Recently, the extraordinary 2-dimentional graphene has been attracting extensive attention in nanoscience and technology. It is one of the leading candidates for various type of applications such as in mobile electronic devices, back-up power supplies and hybrid electric vehicles due to distinctive properties in theoretically high sheet resistance, 1000 Ω/sq., high surface area, 2630 m^2/g, and high capacitance value, 1954 F/g [1–5].

Previously, there are many studies reported that alcohol catalytic chemical vapor deposition (ACCVD) is the most assuring technique in carbon nanotube (CNT) growth because of its wide substrate selectivity, good economic value, and high catalytic reaction [6–11]. The CNT grown from this technique has high potential in electronic device fabrication due to less formation of amorphous carbon and will produce CNTs with high purities [12,13]. Since CNT and graphene is in the same group of materials, thus it is applicable to use alcohol catalytic CVD technique in producing graphene.

The presence of catalyst during the growth process is compulsory for alcohol catalytic CVD technique. Solution technique is a cheap and simple technique to be considered in the preparation of catalyst film. Previously, physical deposition methods are commonly used in catalyst film deposition process [11,14]. In the preparation of active Co_3O_4 films for graphene growth, the most important parameter is the precursor concentration which will determine the quality and structural properties of the as-grown graphene. The ideal precursor solution concentration is attributed to well-distributed precursor material in the solvent without the formation of agglomerates during the coating process.

In employing solution technique in the preparation of catalyst, it is important to control the precursor solution preparation parameter in order to obtain good structural properties of graphene. Therefore, the effect of precursor concentration, aging and spin speed during the spin coating process is presented in this study.

2. Methodology

The active cobalt oxide (Co_3O_4) films were synthesized by using sol gel spin-coated technique. The precursor solution was prepared by diluting 62.27 and 124.54 mg of Co acetate tetrahydrate (Co

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https://doi.org/10.1016/j.diamond.2020.107767
Received 28 December 2019; Received in revised form 30 January 2020; Accepted 23 February 2020
Available online 24 February 2020

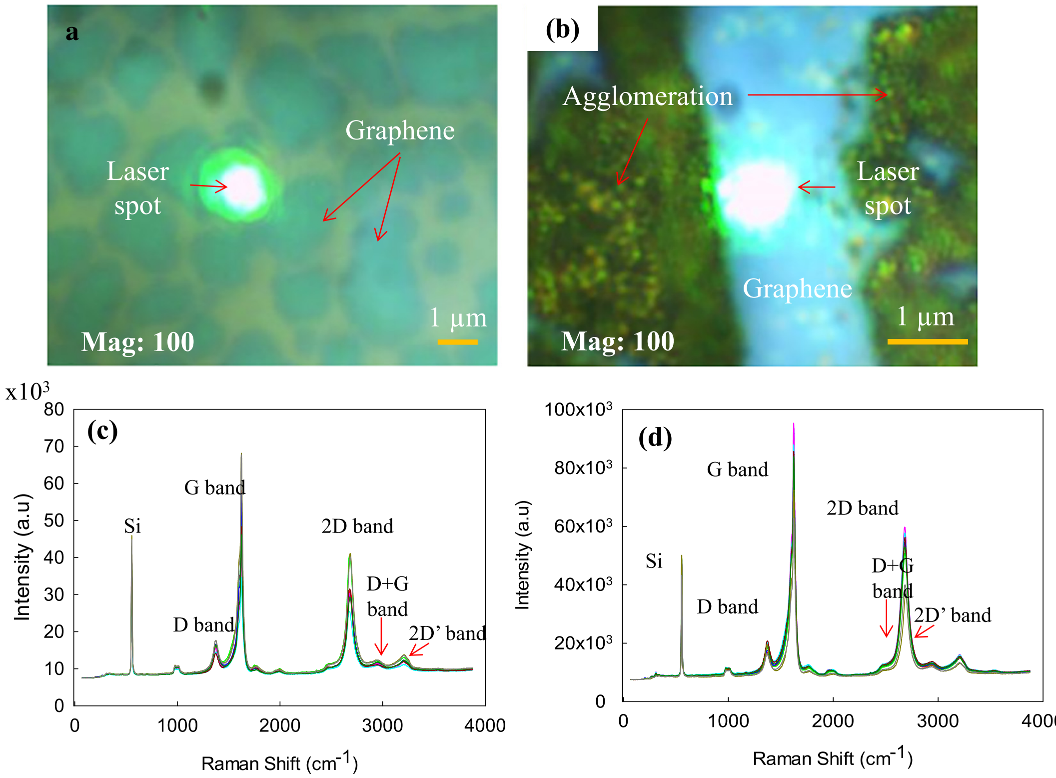

Fig. 1. Optical image and Raman spectra of the as-grown graphene from the active Co_3O_4 film with different concentration of Co acetate tetrahydrate respectively; (a) and (c) 0.025 M, (b) and (d) 0.05 M.

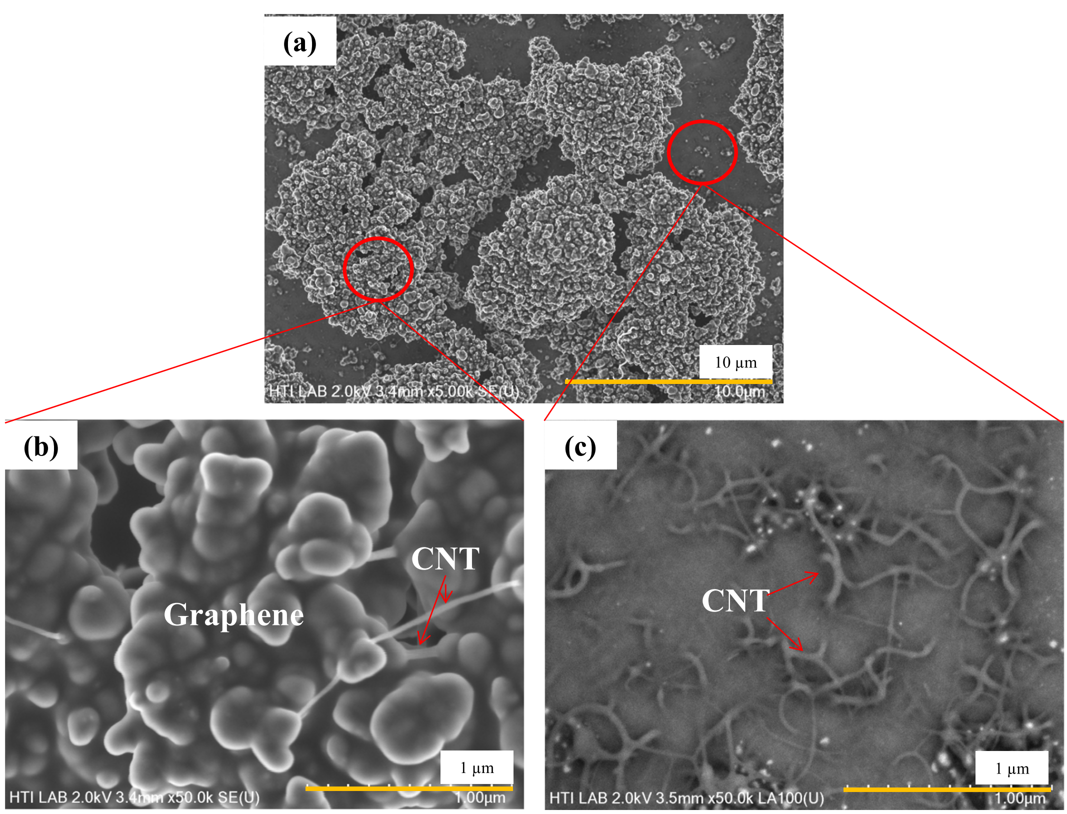

Fig. 2. FESEM images of as-grown graphene from the active Co_3O_4 film captured at various magnifications and spots; (a) as grown area at 5 K magnification, (b) agglomerated area at 50 K magnification, and (c) blue spot at 50 K magnification. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

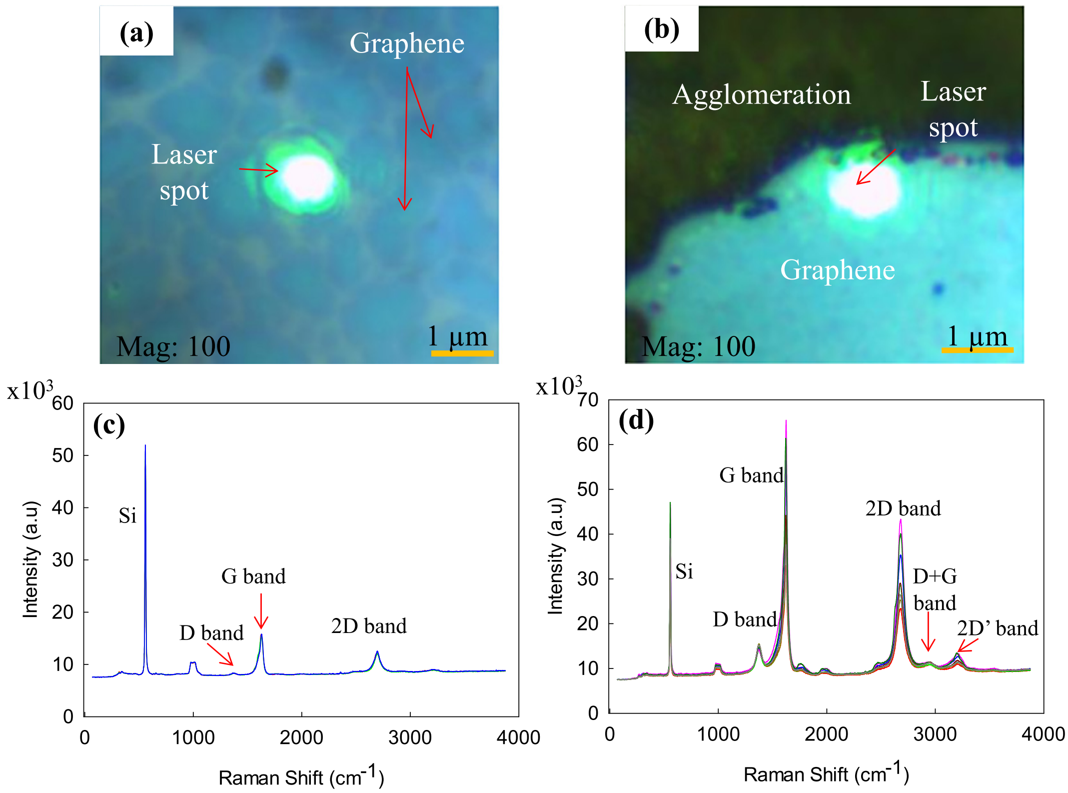

Fig. 3. Optical image and Raman spectra of the as-grown graphene from the active Co_3O_4 film with different concentration of Co acetate tetrahydrate respectively and aged for 4 days; (a) and (c) 0.025 M, (b) and (d) 0.05 M.

$(CH_3COOCH)_{2}.4H_2O$) into 10 mL of absolute ethanol to produce a solution with a concentration of 0.025 and 0.05 mol/L, respectively. The solution was stirred vigorously for 10 min and left for 2 h in ultrasonic bath, thereby leading to the formation of light pink colour solution. To study the effect of aging of the prepared precursor solution on the as-grown graphene, the prepared precursor solution was kept for 4 days in ambient atmosphere.

P-type silicon wafer was cut into 15 mm × 15 mm sizes. The substrates were cleaned by soaking in acetone, left for 10 min in ethanol for sonication, and dried by using nitrogen blow. The non-aging and 4 days aging of precursor solution of Co acetate tetrahydrate/absolute ethanol was spin coated on the cleaned substrates at 2000 rpm and 6000 rpm for 60 s. Subsequently, the spin-coated wafers were preheated at 80 °C for 5 min to vaporize the solvent, thus leaving only Co catalyst films on the wafers. Later, the preheated wafers were placed in the vacuum furnace for annealing process at 450 °C for 1 h to obtain crystalline Co_3O_4 film.

For the alcohol catalytic chemical vapor deposition (ACCVD) process, the prepared catalyst films were placed in a horizontal quartz tube reactor (MTI-OTX 1200X) for graphene growth process. The tube was evacuated using oil-free scroll pump to 0.4 Pa. To prevent the excessive oxidation of Co catalyst, Ar gas was injected into the system at a pressure of 400 Pa concurrently with 5 min of rapid heating and 5 min of second annealing process. Once the annealing process was completed, another Ar gas flow was purged into ethanol closed-tank to vaporize the ethanol and immediately lead off into the system at flow rates of 100–150 sccm. The growth process was conducted at 0.9–1.2 KPa of internal pressure for 5 min. After the growth process, the ethanol gas flow was stopped, and the samples were left for cooling to room temperature. The annealing and growth process was conducted at 900 °C.

The structural properties of graphene were characterized by Raman spectroscopy (Uni-RAM 3500) with laser excitation of 532 nm wavelength (Nd:YAG). The surface morphology and cross section of the samples were characterized by using optical microscope operated with 100 magnifications and field emission scanning electron microscope (FESEM, Hitachi SU8100) operated at 2 KV, respectively.

3. Results and discussion

3.1. Precursor solution concentration effect on the as-grown graphene

Fig. 1(a) shows the optical image of the as-grown graphene synthesized on the active Co_3O_4 film prepared at concentration of 0.025 M. Numerous blue spots were detected on the substrate's surface. The blue spots that expected to be a few layers of graphene are measured in several microns and well distributed on the substrate. However, there are many agglomerates detected on the optical image of the as-grown graphene grown on the active Co_3O_4 films at concentration of 0.05 M (Fig. 1(b)). The blue spots in this figure are indistinct and difficult to capture due to the formation of agglomerates on the catalyst film.

The presence of G-band and 2D-band in the Raman spectrum at 1621 cm^{-1} and 2680 cm^{-1}, respectively, indicates the prove of graphene was grown from ethanol as the carbon feedstock [15]. G-band is specified as the graphitic structure and 2D-band is secondary peak indicates the number of graphene layers. These bands are the fingerprint for the existence of graphene on the sample [16–18]. In order to determine the quality of the as-grown graphene, the ratio of intensity of 2D-band over intensity of G-band was calculated.

There are 9 spots have been spotted from the sample surface for the Raman analysis. The average I_{2D}/I_G ratio for 9 spots of sample prepared from precursor concentration of 0.025 M is 0.632 in which indicates multi-layers of graphene (Fig. 1(c)). However, the average I_{2D}/I_G ratio for 9 spots of sample prepared from precursor concentration of 0.05 M is lower than the previous concentration with the average I_{2D}/I_G ratio value is 0.614 in which also indicates the presence of multi-layers

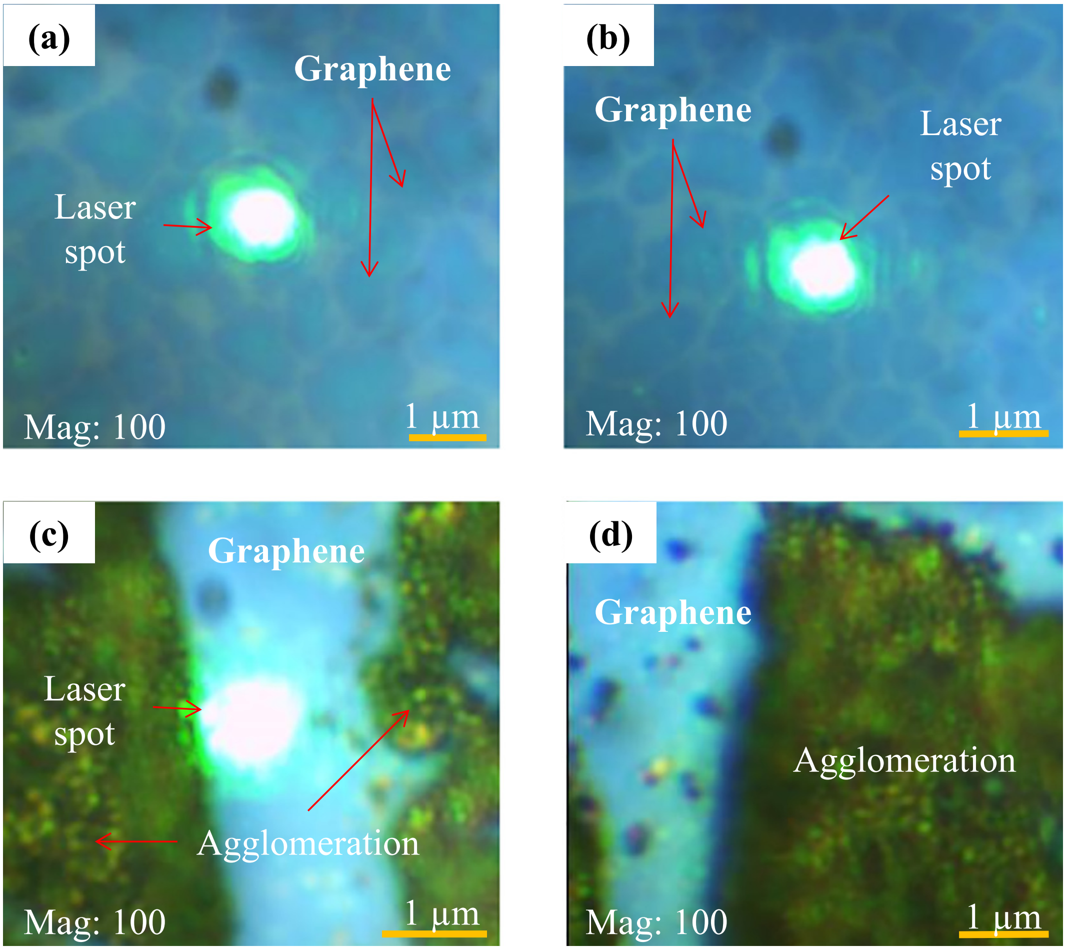

Fig. 4. Optical images of as-grown graphene from the active Co_3O_4 film prepared at various concentrations and spin coated speeds respectively; (a) 0.25 M & 2000 rpm, (b) 0.25 M & 6000 rpm (c) 0.5 M & 2000 rpm and (d) 0.5 M & 6000 rpm.

graphene. Besides, it has higher intensity on G-bands and 2D-bands than 0.025 M concentration (Fig. 1(d)). The narrow peak of G-bands and 2D-bands also indicates the good structure of graphene formed on the substrate's surface. Hence, even though the concentration of 0.05 M tends to form agglomerate, the exhibited peaks are stronger than that of concentration 0.025 M.

Since the Raman analysis on the agglomerates and the blue area of sample at concentration of 0.05 M revealed the presence of graphene, the morphology of the as-grown graphene is then further confirmed by using the field emission scanning electron microscope (FESEM) image and the result is shown in Fig. 2(a) in below.

Based on the FESEM image of the agglomeration area, random shapes of graphene structures along with a few stripes of carbon nanotube (CNT) that connected from one graphene structure onto another is observed (Fig. 2(b)). The blue spots that were observed in the optical image showed the presence of CNT (Fig. 2(c)). Graphene structures might present on the background of the Fig. 2(c) because strong 2D-bands are also exhibited on the Raman spectrum. This indicated that the chemical vapor deposition (CVD) processing temperature at 900 °C is not enough to eliminate the CNT from the substrate. Higher CVD processing temperature is necessary in order to make sure the sole presence of graphene structure on the surface. Somehow, the existence of CNT might be helpful in a certain application [19–21]. This is an interesting finding for those who may need a mixture of graphene and CNT in their compositions.

3.2. Aging effect on the as-grown graphene

In sol-gel method, aging process is an important step to make sure the precursors' solution is chemically well-reacted between them. In particular, during the reactive side of precursor material is ready to be coated and bonded onto the substrate's surface [22–24]. In this study, the precursor solution prepared at concentration of 0.025 and 0.05 M is kept for 4 days before spin coating process.

Based on the optical images in Fig. 3(a), the blue spots are observed. The blue spots indicate the presence of graphene structures which has been confirmed by Raman analysis shown in Fig. 3(c). The G-band and 2D-band are presented in the spectra. From Fig. 3(d), it was found that the intensity of both bands was not as strong as the intensity of sample prepared at the concentration of 0.05 M. The agglomerates are observed on optical image of sample prepared at concentration of 0.05 M (Fig. 3(c)). The average I_{2D}/I_G ratio for sample prepared at concentration 0.025 and 0.05 M is 0.787 and 0.674, respectively. Based on this result, precursor solution prepared at concentration 0.05 M is more stable than that of 0.025 M. The agglomeration problem can be solved with the modification on the other parameter such as annealing parameter and/or by adding compatible surfactant into the precursor solution.

3.3. Spin speed effect on the structure properties of the as-grown graphene

Fig. 4(a), (b), (c) and (d) depict the optical images of the as-grown graphene synthesized from the active Co_3O_4 film prepared from precursor solution with concentrations of 0.025 and 0.05 M, accordingly.

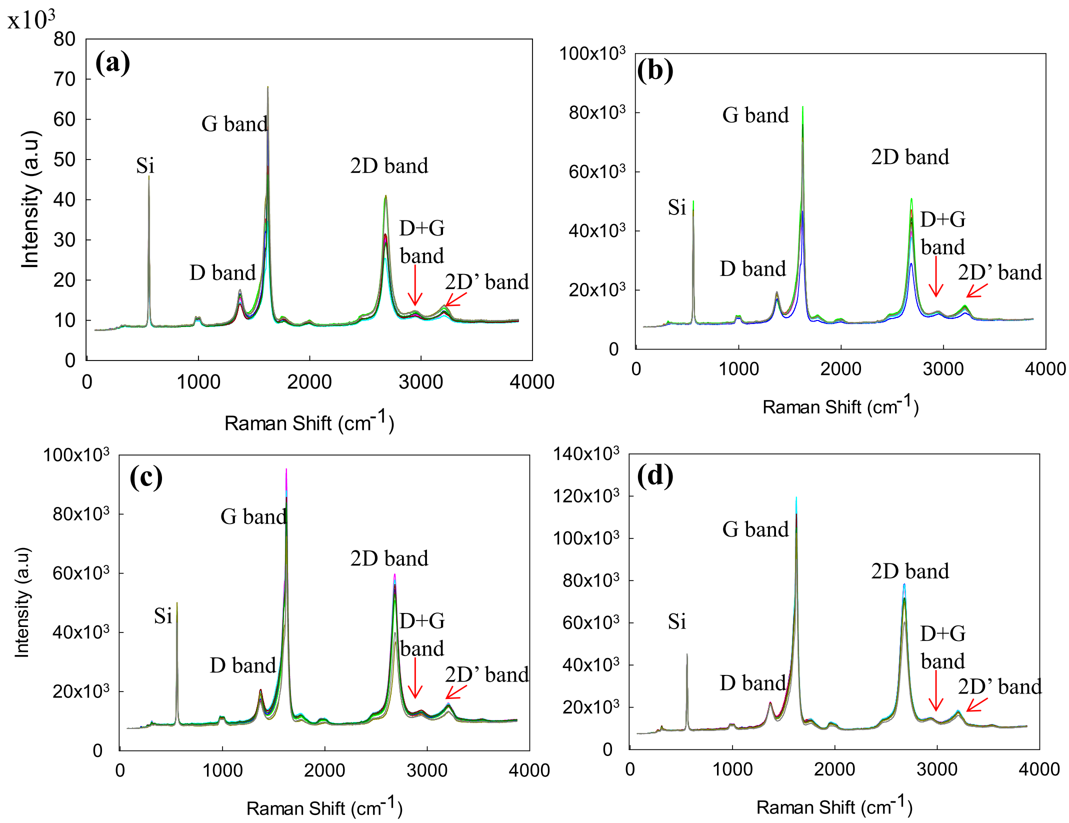

Fig. 5. Raman spectra of as-grown graphene from the active Co_3O_4 film prepared with various concentrations and spin coated speeds respectively; (a) 0.025 M & 2000 rpm and (b) 0.025 M & 6000 rpm at (c) 0.05 M & 2000 rpm and (d) 0.05 M & 6000 rpm.

Fig. 4(a) and (c) is the optical images of the as-grown graphene grown from the active Co_3O_4 film spin coated at 2000 rpm, and Fig. 4(b) and (d) are the samples spin coated at 6000 rpm. There is no different on the morphology of the as-grown graphene spin coated at 2000 rpm and 6000 rpm for both concentrations. The blue spots also can be observed on samples prepared at concentration of 0.025 and 0.05 M. Based on these results, it can be suggested that there is no effect of the spin speed on the morphology of the as-grown graphene.

Fig. 5 shows the effect of spinning speed on the structural properties of the as-grown graphene. The average I_{2D}/I_G ratio for samples prepared at concentration 0.025 with spin speed of 2000 rpm and 6000 rpm are 0.634 and 0.611, respectively. The average I_{2D}/I_G ratio for the samples prepared at concentration of 0.05 M with spin speed of 2000 rpm and 6000 rpm are 0.614 and 0.679, respectively. These results indicate that the as-grown graphene are multi-layers graphene. The I_{2D}/I_G ratios seem in range of 0.6. Thus, it can be concluded that the spin speed has no effect on the structural properties of the as-grown graphene. Thus, this factor can be neglected.

4. Conclusions

The graphene has been successfully synthesized by alcohol catalytic chemical deposition technique. Agglomerates were formed in sample with 0.05 M of Co acetate tetrahydrate, however it was found that the Raman peaks intensity increased as compared to the 0.025 M sample. This is then correlated to the graphene growth. The precursor with 0.05 M has an acceptable chemical stability though aged for 4 days and contributed to the growth of graphene. The spin coating speed was found not to affect the graphene growth at all.

For the aging effect, concentration 0.025 M shows unstable condition as compared to concentration 0.05 M when the precursor solution is aging for 4 days. This is due to the weak Raman peaks observed on Raman spectrum. Besides, both morphological and structural properties of the as-grown graphene show that there is no effect on the variation of spin speed during the spin coating process. In short, precursor solution prepared at concentration of 0.05 M is the suitable parameter to be considered in order to get good structural properties of the as-grown graphene. As suggested earlier, some modification on other parameter might be needed to avoid the agglomeration problem.

CRediT authorship contribution statement

Mohd Asyadi Azam: Conceptualization, Writing - original draft. **Mohd Fareezuan Abdul Aziz:** Writing - review & editing. **Nor Najihah Zulkapli:** Writing - original draft, Methodology. **Ghazali Omar:** Supervision. **Rose Farahiyan Munawar:** Writing - review & editing. **Mohd Shahadan Mohd Suan:** Investigation. **Nur Ezyanie Safie:** Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Authors would like to thank Universiti Teknikal Malaysia Melaka (UTeM) for supporting this research.

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