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Analysis of Metal Catalyst Etching in Graphene Transfer Process

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Abstract
Before graphene can be applied to a device, it should first be transferred from the surface of the catalyst to the surface of the silicon substrate. The most commonly used transfer methods start with adhesion on a polymethyl methacrylate film. This film supports the graphene film and prevents folding while the copper catalyst is etched away in ferric chloride ($FeCl_3$) solution. In this study, we analyzed the molarity and temperature of $FeCl_3$ during the graphene transfer process. Raman spectroscopy and scanning electron microscopy were used to characterize the transferred graphene by its number of layers, uniformity, and produced defects. We found that optimum parameters of $FeCl_3$ are required to produce high-quality graphene with low defects. Results show that molarity of 0.5 M and a temperature of 40 °C produced the best quality graphene that yielded monolayer graphene and the best surface uniformity. This etchant optimization study will provide a new understanding of the production of a better transferred graphene.

Keywords: graphene, transfer process, PMMA film, molarity, etchant, $FeCl_3$

INTRODUCTION

Graphene is a single atomic layer of carbon that is densely packed into a benzene-ring structure (K. S. Novoselov, 2004) arranged in a two-dimensional (2D) crystal (Novoselov et al., 2005b). Numerous methods have been developed to prepare graphene (Yang et al., 2013) since its first mechanical exfoliation from highly ordered pyrolytic graphite in 2004 by Novoselov et al. (K. S. Novoselov, 2004). Graphene has been attracting much attention because of its fascinating mechanical properties [high elasticity (Lee, 2008) and nano-electromechanical system modulation (J. Scott Bunch, 2008)], electronic properties [tunable energy gap (Han Y. Melinda, 2007), ultrahigh electron mobility of 200,000 $cm^2\ V^{-1}\ s^{-1}$ (Bolotin et al., 2008), and quantum electrodynamics (Novoselov et al., 2005a)], high thermal conductivity (Balandin A.A., 2008), optical properties for photodetector applications (Pospischil et al., 2013), ultra-wide bandwidths for exa-scale (10^{18}) computing systems (Kim et al., 2011), and optical transparency range [97%–98% (Nair R. R., 2008)]. An attractive alternative to the mechanical exfoliation method is to synthesize graphene by growing it directly on a surface, which can be achieved in two processes. One method is epitaxial growth of graphene on a hexagonal substrate of silicon carbide (SiC). This thermal decomposition process involves heating the sample in an ultra-high vacuum to temperatures between 1273 and 1773 K, which causes Si to sublimate, leaving a carbon-rich surface. Another method for the direct growth of graphene is chemical vapor deposition (CVD) (Tetlow et al., 2014). In this process, graphene is grown by exposing an Ni film to a gas mixture of H_2, CH_4, and Ar at approximately 1000 °C (Kim et al., 2009). Recent developments in high-quality CVD (Bae et al., 2010) graphene synthesis facilitate the wafer-scale integration of Si and other materials with graphene. It is well known that the quality of CVD graphene strongly dependent on the growth condition (Zhou et al., 2013). CVD growth techniques are still under very active research (Diaz-Pinto et al., 2012).

To fabricate devices such as field-effect transistors or transparent conducting electrodes, graphene should be transferred onto different substrates with high quality, high efficiency, low cost, and large area (Chen et al., 2013). This process also eases the characterization of the transferred graphene by its structural defect and identification of the number of carbon layers by Raman spectroscopy and surface morphology using scanning electron microscopy (SEM).

Various methods have been developed to transfer graphene onto substrates. The most commonly used transfer methods rely on polymethyl methacrylate (PMMA) film (Li X, 2009). This film is used to support the graphene film and prevent folding while the metal catalyst is being etched (Chen et al., 2013). PMMA has also been widely used to transfer CVD-grown graphene to target substrates using direct transfer and transfer with carrier processes (Ren et al., 2012). Haveneret al. (Havener R. W., 2012) synthesized graphene on a copper (Cu) catalyst using spin coating with PMMA liquid. The catalyst was then etched in $FeCl_3$ and washed in deionized (DI) water to remove the etchant residues. Afterwards, the sample was transferred onto the substrate and heated to remove the water. Finally, the graphene sample was soaked in acetone solution and dried with nitrogen gas. However, the parameter of the etchant molarity and temperature was not discussed.

Li et al. (Li X, 2009) used graphene film on Cu foil drop-coated with PMMA, which was subsequently cured at 180 °C for 1 min. The metal substrate was then etched by an aqueous solution of iron nitrate for approximately 12 h. Then, the PMMA and graphene stack was washed with DI water, placed on the target substrates, and dried. After the transfer to the targeted substrate, a small amount of the liquid PMMA solution was dropped onto the sample to dissolve the pre-coated PMMA. The PMMA film was then slowly cured at room temperature for around 30 min and then dissolved by acetone. Result shows that the graphene transfer process was improved by introducing a second PMMA coating after the graphene was placed on the Si substrate. However, this step will produce more chemical residues on the sample.

In this paper, we explored the $FeCl_3$ molarity and temperature to evaluate the properties of the transferred graphene because these etchant parameters were rarely considered in previous studies. These parameters play an important role in the production of high-quality graphene during the transfer process.

EXPERIMENTAL METHOD

Transfer Process

A CVD-synthesized commercial graphene, which was grown on a Cu foil (20 µm thick), was used as the sample. The sample size was 4 cm × 4 cm, and prior to the transfer process, the samples were cut into 1 cm × 1 cm to ease the transfer process. The sample was transferred to a Si substrate of a 300 nm thick SiO_2 layer (Si/SiO_2) via a wet etching process. This process was assisted by a thin layer of PMMA (MicroChem 950 PMMA, 4% in Anisole). PMMA was first spin-coated to the side of the grown graphene. Then, the Cu foil was removed by immersing the stack of exposed Cu side to $FeCl_3$ solutions at different molarities (0.5, 1.0, 1.5, 2.0, and 2.5 M) and different temperatures (25, 40, 55, 70, and 85 °C). The color of the etching solution turned from brownish to dark brownish when the Cu foil was etched. The entire process was performed under a fume hood because the reaction released a corrosive vapor. After the Cu foils were completely etched away, the PMMA-supported graphene was scooped and transferred to DI water a few times to remove any of the Cu residues and PMMA film. Our transfer process of graphene on the substrate is schematically shown in Figure 1.

Characterization

The surface uniformity of the transferred graphene on the SiO_2/Si substrate was characterized using SEM (JEOL JSM-7500F). In addition, the graphene sample was characterized using AFM-Raman system (NT-MDT). A Raman spectrometer with 473 nm laser excitation (~2 µm spot size) was utilized to investigate the number of graphene layers. The wave number was calibrated using the 520.5 cm^{-1} peak of Si.

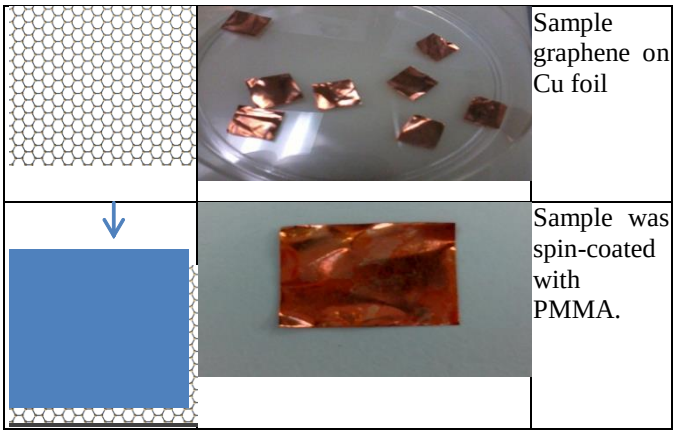


Figure 1: Schematic and photograph representation of graphene transfer process on the Si substrate.

RESULT AND DISCUSSION

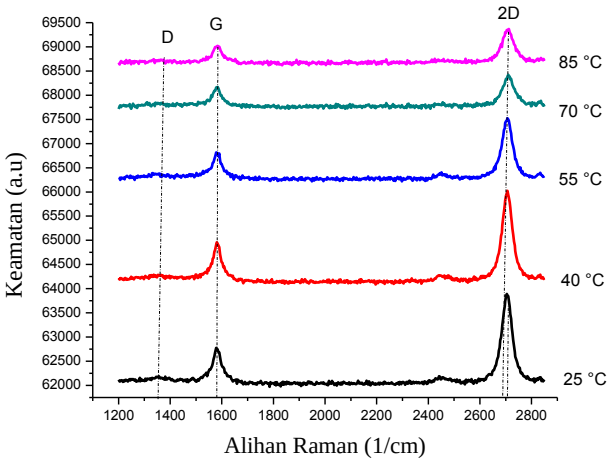
The sample was characterized using Raman spectroscopy to investigate its structural defects and number of graphene layers. For Raman characterization, three significant peaks were found: 2D (~2699 cm^{-1}), G (~1584 cm^{-1}), and D (~1352 cm^{-1}) peaks. The 2D peak represents the second-order defect peak, G is the graphitic peak, and D is the defect peak (Ferrari and Basko, 2013). The intensity of the 2D peak over G peak provides a good estimation of the number of layers in their graphene samples. From the literature, $I_{2D}/I_G>2$ shows a monolayer graphene, and a multilayer graphene is indicated if I_{2D}/I_G is <2 (Juang et al., 2010). Nonetheless, the ratios can change due to sample annealing, doping and variation of laser focusing. Meanwhile, to study the structural defect, an intensity of zero for I_D/I_G is considered an ideal graphene (Regmi et al., 2012). However, ideal graphene is very difficult to achieve. The graphene sample was analyzed using SEM to investigate the surface structure of the transferred graphene.

Table 1 shows the data of the transferred graphene with varied $FeCl_3$ molarities and temperatures. When the molarity and the temperature of the etchant increased, the intensity of I_{2D}/I_G

decreased, contrary to the increase in intensity of I_D/I_G. This finding also shows that when the molarity and temperature of the etchant increased, the number of layers decreased, because I_{2D}/I_G is 2.388 (I_{2D}/I_G>2 is monolayer) at 0.5 M $FeCl_3$ and 25 °C. For the sample defect, I_D/I_G=0.10at 0.5 M $FeCl_3$ and 25 °C, which shows that the transferred graphene had low defect (I_D/I_G<0.3).

Table 1: Raman data shift for molarity and temperature of etchant from 0.5 M to 2.5 M and 25 °C to 85 °C, respectively

No.	Molarity (M)	Temperature (°C)	I_{2D}/I_G	I_D/I_G
1	0.5	25	2.388	0.10
2		40	2.271	0.14
3		55	1.855	0.15
4		70	1.548	0.43
5		85	1.472	0.38
6	1.0	25	2.210	0.17
7		40	2.217	0.28
8		55	2.166	0.11
9		70	1.821	0.17
10		85	1.811	0.35
11	1.5	25	2.445	0.07
12		40	2.588	0.05
13		55	2.170	0.28
14		70	2.055	0.24
15		85	1.143	0.48
16	2.0	25	2.160	0.20
17		40	2.145	0.22
18		55	2.045	0.15
19		70	2.078	0.41
20		85	1.920	0.40
21	2.5	25	1.450	0.32
22		40	1.920	0.20
23		55	1.082	0.36
24		70	0.736	0.34
25		85	0.680	0.39



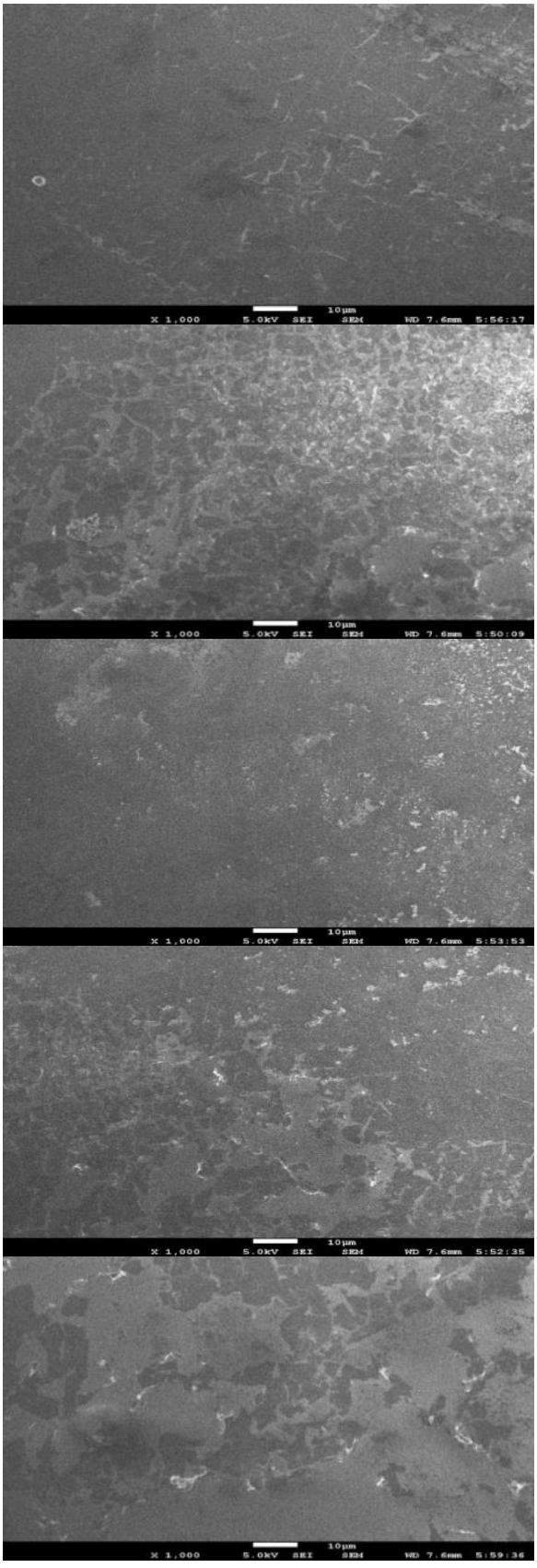
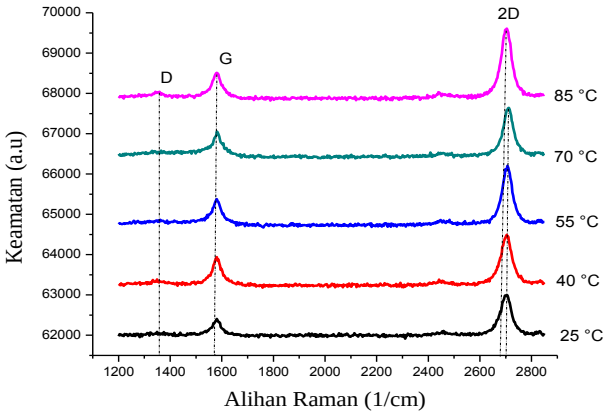
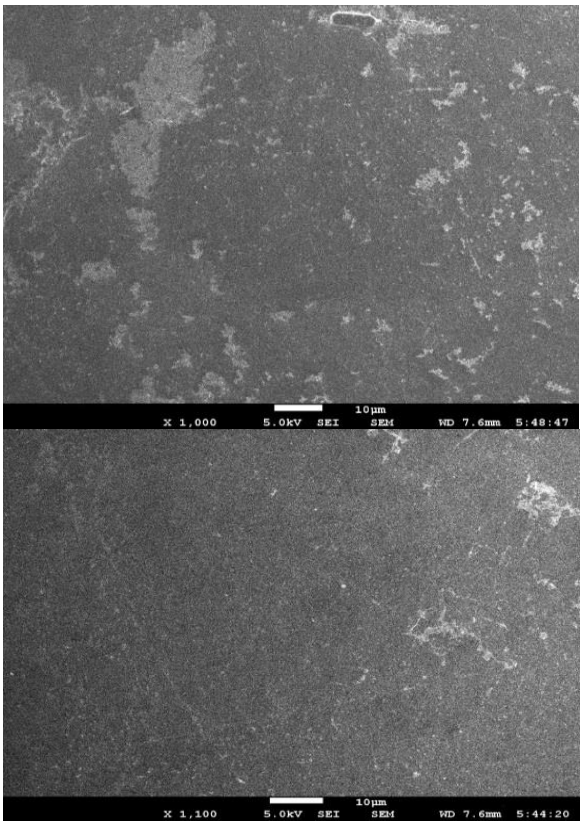


Figure 2: (a) Raman spectra and (b) SEM images of the surface uniformity of the transferred graphene under 0.5 M $FeCl_3$ from 25 °C to 85 °C.

Figure 2(a) shows the Raman spectra of the transferred graphene under 0.5 M $FeCl_3$ from 25 °C to 85 °C. A total of 5 samples were analyzed using Raman spectroscopy and SEM. At 0.5 M $FeCl_3$ and etchant temperatures of 25 and 40 °C, the sample produced a monolayer of transferred graphene. At 55, 70, and 85 °C, the sample produced multilayer graphene. Thus, increased etchant molarity and temperature will result in multilayer graphene. For the defect level, lower molarity and temperature resulted in minimal defect.

Figure 2(b) shows the SEM images of the surface uniformity under 0.5 M $FeCl_3$ from 25 °C to 85 °C. At 25 °C, the surface was more uniform and exhibited low defect. Meanwhile, a non-uniform surface was observed at the highest temperature (85 °C). The darker region of color contrast was due to thicker graphene layers, which is similar to the slightly folded graphene that possibly appeared as a wrinkle. The morphological evolution of graphene with different defect densities can be tuned by altering the etchant molarity and temperature.





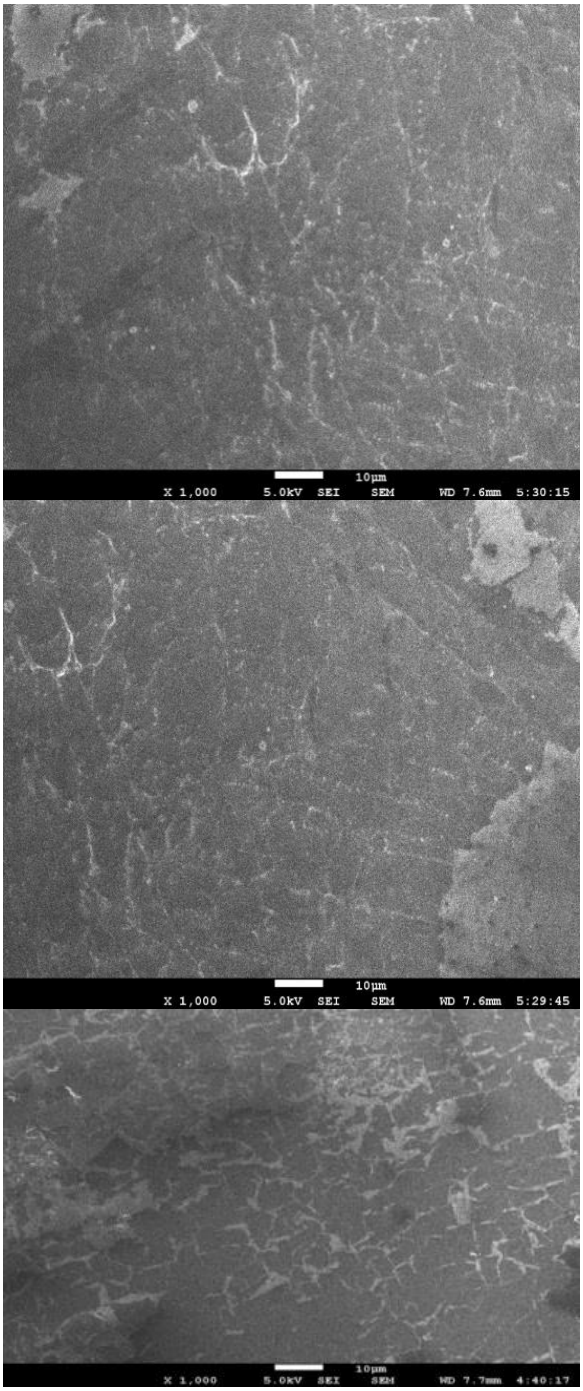
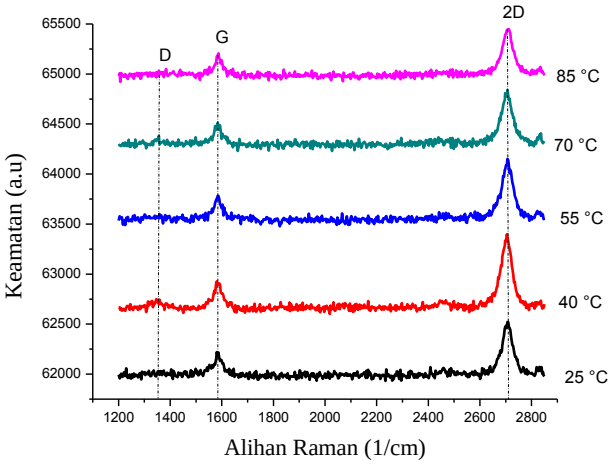


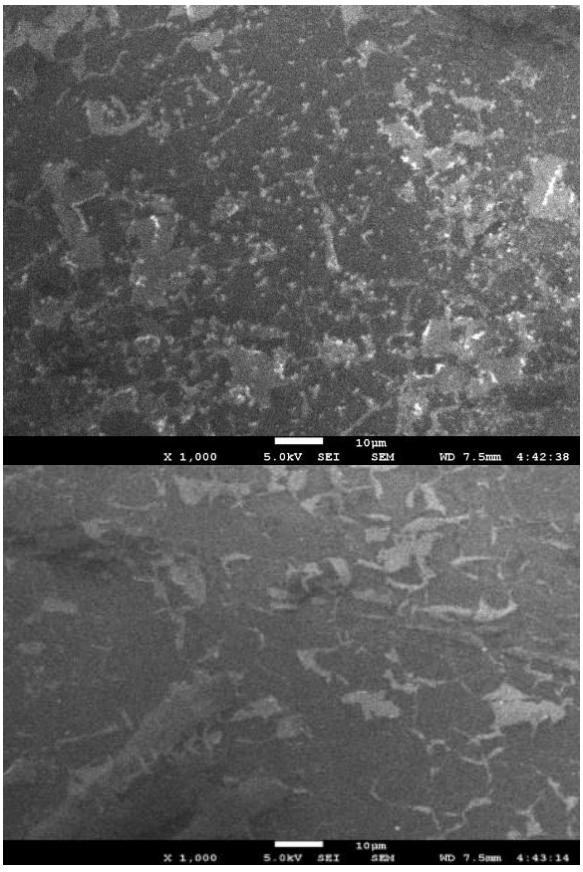
Figure 3: (a) Raman spectra and (b) SEM images of the surface uniformity of the transferred graphene under 1.0 M $FeCl_3$ from 25 °C to 85 °C.

Figure 3(a) shows the Raman spectra of the transferred graphene under 1.0 M $FeCl_3$ from 25 °C to 85 °C. The samples were analyzed using Raman spectroscopy and SEM. At 1.0 M $FeCl_3$ and etchant temperatures of 25, 40, and 55 °C, the sample produced a monolayer of transferred monolayer graphene. At 70 and 85 °C, the sample produced multilayer graphene. Thus, multilayer graphene is produced when the molarity and temperature of the etchant are increased. For the defect level, lower molarity and temperature resulted in minimal defect. At

85 °C, I_D/I_G was 0.35, which shows that it had the highest defect.

Figure 3(b) shows the SEM images of the surface uniformity under 1.0 M $FeCl_3$ from 25 °C to 85 °C. At 25 °C, the surface was more uniform and had low defect. Meanwhile, at 85 °C, the surface was non-uniform and darker. This result suggests that the number of layers increased at 85 °C.





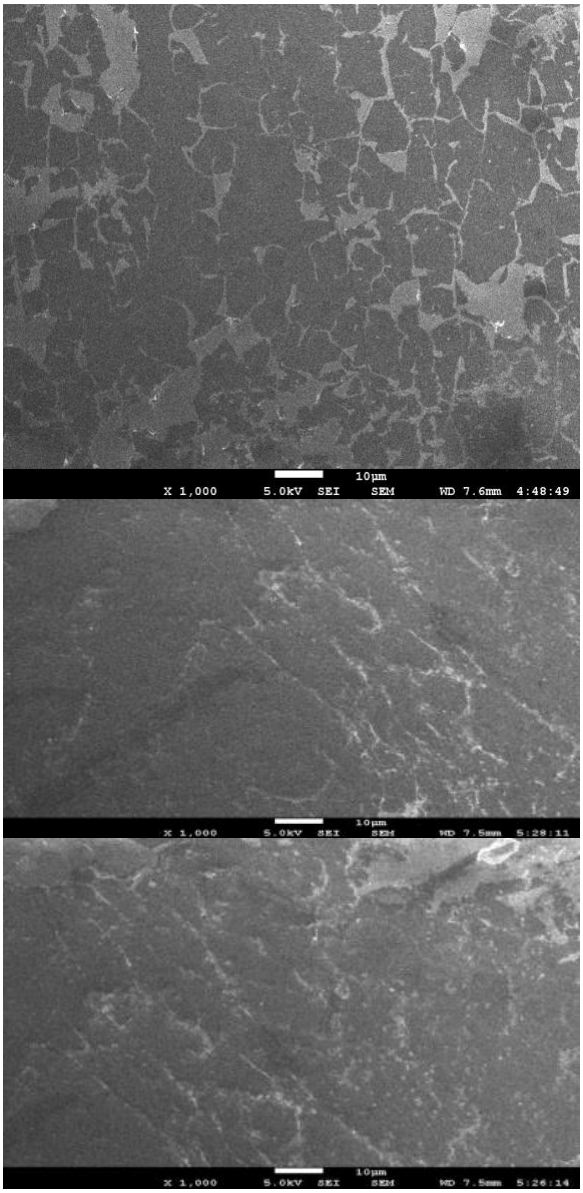
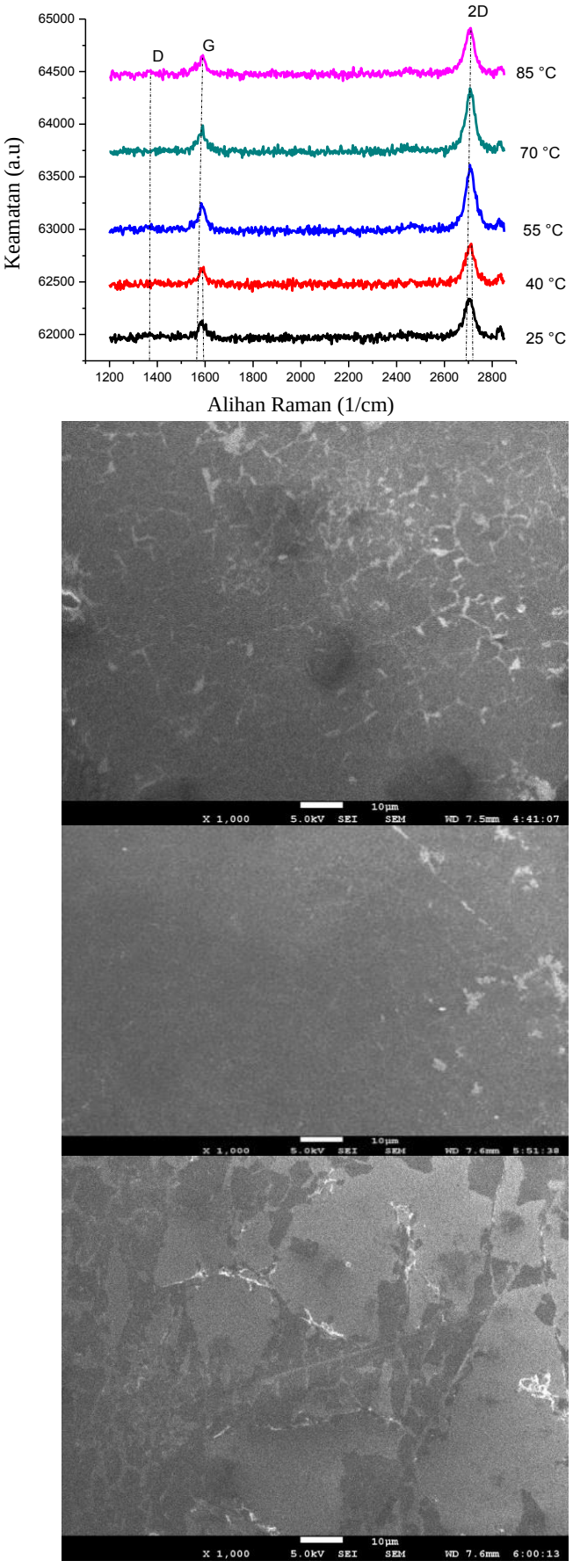


Figure 4: (a) Raman spectra and (b) SEM images of the surface uniformity of the transferred graphene under 1.5 M $FeCl_3$ from 25 °C to 85 °C.

Figure 4(a) shows the Raman spectra of the transferred graphene under 1.5 M $FeCl_3$ from 25 °C to 85 °C. The samples were analyzed using Raman spectroscopy and SEM. At 1.5 M $FeCl_3$, the sample produced multilayer graphene at 85 °C. Results showed that a monolayer of transferred graphene was produced at 25, 40, 55, and 70 °C. At 85 °C, I_D/I_G=0.48, which showed that it had the highest defect.

Figure 4(b) shows the SEM images of the surface uniformity under 1.5 M $FeCl_3$ from 25 °C to 85 °C. At 25 °C, the surface was more uniform and had low defect. Meanwhile, at 85 °C, a non-uniform and darker surface was observed. Thus, the number of layers increased at 85 °C.



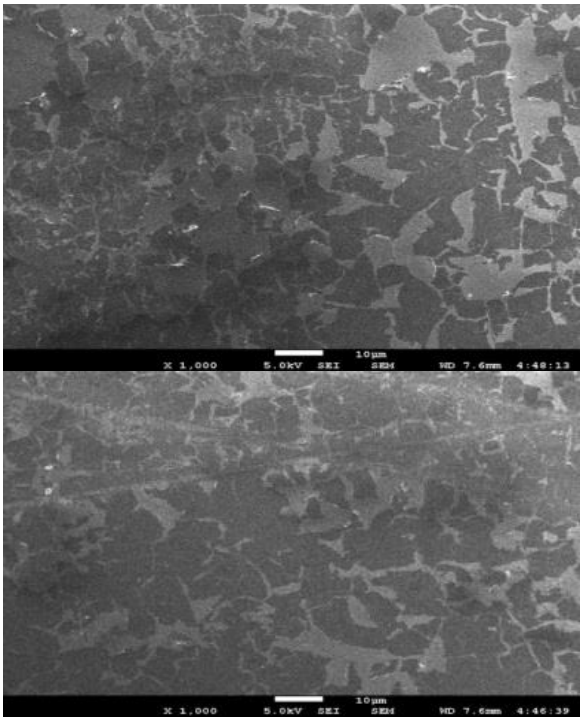
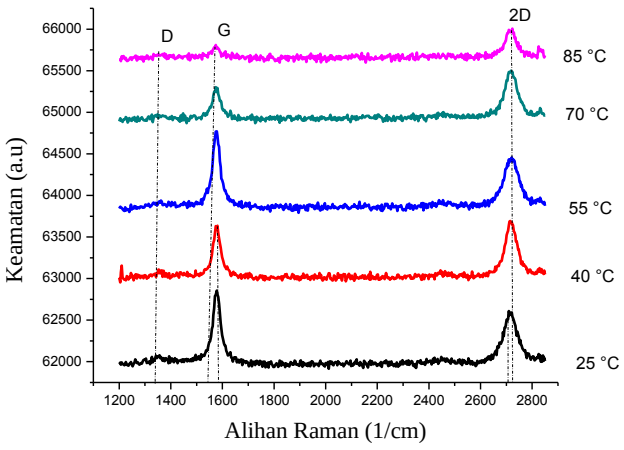


Figure 5: (a) Raman spectra (b) SEM images of the surface uniformity of the transferred graphene under 2.0 M $FeCl_3$ from 25 °C to 85 °C.

Figure 5 (a) shows the Raman spectra of the transferred graphene under 2.0 M $FeCl_3$ from 25 °C to 85 °C. The samples were analyzed using Raman spectroscopy and SEM. At 2.0 M $FeCl_3$ and etchant temperatures of 25, 40, 55, and 70 °C, the I_{2D}/I_G values were 2.160, 2.145, 2.045, and 2.078, respectively. A monolayer graphene is produced when I_{2D}/I_G >2. At 85 °C, multilayer graphene was observed. For the defect level, I_D/I_G=0.40 at 85 °C, which indicates the highest defect.
Figure 5 (b) shows the SEM images of the surface uniformity of the transferred graphene under 2.0 M $FeCl_3$ from 25 °C to 85 °C. At 25 °C, the surface was more uniform and had less defect. A non-uniform and darker surface was observed at 85 °C. These findings imply that the number of layers increased at 85 °C.



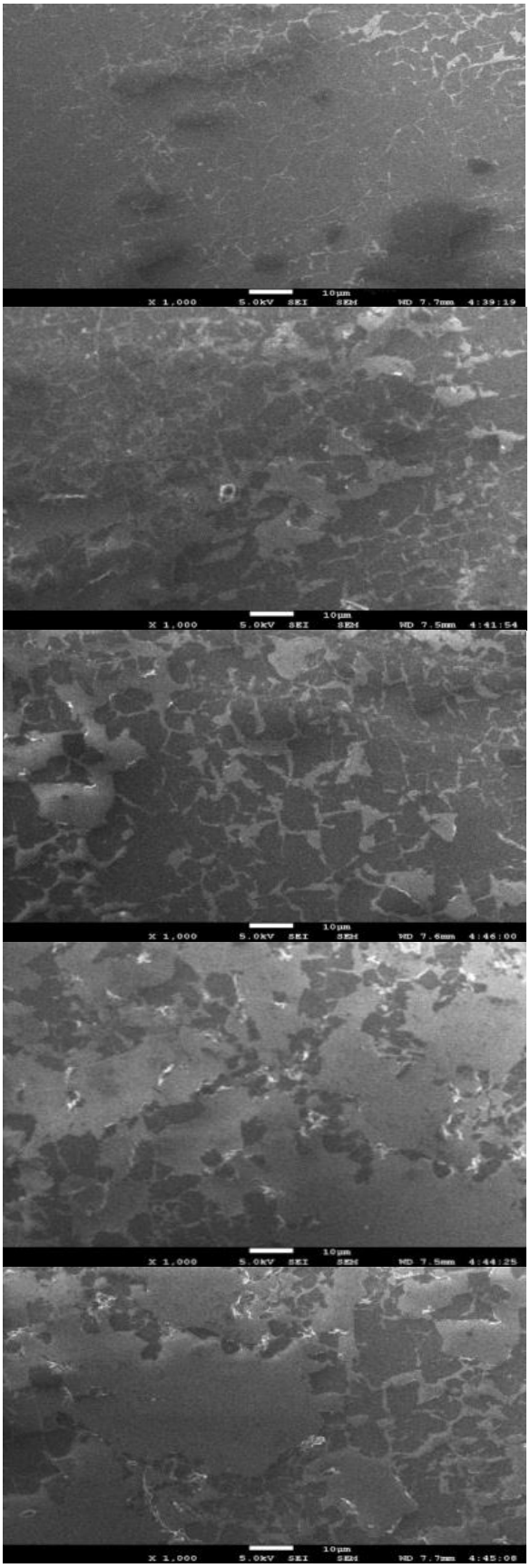


Figure 6: (a) Raman spectra and (b) SEM images of the surface uniformity of the transferred graphene under 2.5 M $FeCl_3$ from 25 °C to 85 °C.

Figure 6(a) shows the Raman spectra of the transferred graphene at 2.5 M $FeCl_3$ from 25 °C to 85 °C. At 2.5 M $FeCl_3$ and at all temperatures, multilayer graphene was produced because all values of $I_{2D}/I_G<2$. For the defect level, lower molarity and temperature resulted in minimal defect. At 85 °C, $I_D/I_G=0.39$, which indicates the highest defect.

Figure 6(b) shows the SEM images of the surface uniformity of the transferred graphene under 2.5 M $FeCl_3$ from 25 °C to 85 °C. The darker region of the color contrast was due to thicker graphene layers, which is similar to the slightly folded graphene that possibly appeared as a wrinkle. From the image, the surface is not uniform at lower and highest temperatures.

CONCLUSION

In summary, graphene sample on Cu foil was transferred onto SiO_2 substrate using PMMA-assisted technique. $FeCl_3$ was used as the solution to etch away the Cu foil. The effects of the molarity and the temperature of the etchant were compared. The parameters were optimized to produce high-quality graphene on the Si substrate. Raman spectroscopy and SEM were used to characterize the transferred graphene. Transferred graphene with etchant molarity of 0.5 M and temperature of 40 °C produced the best-quality graphene. The optimized parameters yielded monolayer graphene and better surface uniformity with the highest I_{2D}/I_G value of 2.588 and lowest I_D/I_G value of 0.05.This etchant investigation will provide an improved understanding of transferred graphene behavior on a Si substrate.

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