Effect of Pulsed Light Irradiation on Patterning of Reduction Graphene Oxide-Graphene Oxide Interconnects for Power Devices

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Abstract: Reduction graphene oxide (r-GO) lines on graphene oxide (GO) films can be prepared by a photocatalytic reduction and photothermal reduction method. A mechanism of partial GO reduction by pulsed photon energy is identified for preparing patterned rGO-GO films. The photocatalytic reduction method efficiently reduces GO at low photon energies. The successful production of a patterned rGO-GO film without damage by the photo thermal reduction method is possible when an energy density of 6.0 or 6.5 J/m² per pulse is applied to a thin GO film (thickness: 0.45 µm). The lowest resistance obtained for a photo-reduced rGO line is 0.9 kΩ sq⁻¹. The GO-TiO₂ pattern fabricated on the 0.23 µm GO-TiO₂ composite sheet through the energy density of each pulse is 5.5 J/m² for three pulses.

Keywords: graphene pattern; pulsed photon energy; photocatalyst

1. Introduction

In recent years, decreasing the through silicon via (TSV) size has caused a rapid increase in the aspect ratio (AR) during pitching in technology nodes below 10 nm [1], resulting in poor film coverage of barrier/seed layers owing to thermomechanical stress [2]. Problematic resistance (R)–capacitance (C) delays with increased resistance caused the boundary scattering and shorter mean free paths that result from using nano-thick copper as a reasonable material for interconnections [3–5]. For overcoming this drawback, the development of new materials to replace copper is necessary [6]. Nanocarbon materials, which are semiconductors with band gaps of 0 eV, possess excellent properties, including high electron transfer rates, superior thermal conductivities [7], low costs [8], flexibility, and high surface ratio area [9,10]. Nanocarbon materials have received considerable attention for various applications, such as flexible electronic devices [11], graphene-based sensors [12], Li-ion batteries [13], and supercapacitors [14–19]. Nanocarbon semiconductors in terms of vertical carbon nanotube (CNT) interconnection and horizontal graphene lines have received increased attention to solve this disadvantage [20]. However, to realize commercially viable nanocarbon semiconductors, methods for restricting graphene defects and CNT structures are required. In particular, the graphene line should be used as a substrate and (or) line by controlling the electric properties by patterning the graphene. Therefore, graphene patterning is a very important problem.

Recently, patterning technology of graphene oxide (GO) that has insulation properties due to oxygen-containing functional groups is attracting attention in the reduction process [21–23]. In particular, the reduction process using photon energy has advantages that make it possible to make a flexible film by using a polymer substrate such as polyethylene phthalate (PET), because it has a very short process time and instantaneously generates thermal energy so that it does not cause thermal damage to the substrate [24,25].
Generally, the photon energy-based GO reduction can be divided into two categories: Photo catalysis reduction and photo-thermal reduction. Photo catalysis produces a hole ($h^+$) in the valance band and electron ($e^-$) in the conduction band when it absorbs the photon energy above the bond gap. This results in a strong reduction-oxidation reaction. Photo-thermal reduction uses thermal energy generated by the conversion of photon energy and can be reacted by various light sources such as a camera xenon flash, UV light, IR light, and laser beams. A GO pattern with less damage and high resolution is possible when using UV light and laser beams. In particular, graphene patterning technology using Extreme ultraviolet (EUV) is attracting attention [26–29]. EUV has a very short wavelength of 13.5 nm, which can be expected to have greatly improved resolution. However, unlike pulsed photo irradiation, GO reduction using an excimer laser and EUV requires the use of a vacuum environment. On the other hand, the most effective method for reducing GO has been indicated. In this study, we aim to make the graphene line damage free by understanding pulsed energy and the photo catalyst reaction [25,30–35]. We use the instantly irradiating strong light energy method using a pulsed system such as camera xenon flash. However, the photon thermal reduction via pulsing may cause damage due to the rapid volume expansion of the GO film [36–40].

In this study, a patterning technique is proposed to produce rGO lines on GO films using irradiated pulsed energy and photo catalyst reaction. It is necessary to determine the optimal pulsed energy density to minimize rGO line defects and decrease the resistance of the obtained rGO lines.

2. Material and Methods

2.1. Synthesis of GO

All reagents were just used for analyzing and were not purified chemicals. GO was fabricated by a modified Hummer’s method [41,42]. Graphite powder (4 g, >100 mesh, Sigma Aldrich, St. Louis, MO, USA) and NaNO$_3$ (2.0 g) were poured into 92 mL of sulfuric acid with stirring at 400 rpm for 15 min. The temperature was maintained at 0 °C by using an ice bath. KMnO$_4$ powder (6.0 g) [43,44] was slowly added to the mixture, which was then stirred for 1 h, with the temperature of the mixture maintained at ~20 °C. After stirring, the mixture was removed from the ice bath and stabilized for 2 h. Subsequently, 184 mL of deionized (DI) water was added slowly over 15 min, with the temperature maintained at ~98 °C. Then, 560 mL of DI water with 20 mL of H$_2$O$_2$ (30 wt.% aqueous solution) was added. The product was isolated by vacuum filtration and washed until the pH reached 7 [45,46]. The residue was sonicated for 2 h and then filtered using a metal US Standard Testing Sieve (300 µm). Finally, the obtained GO was vacuum dried at 60 °C.

2.2. Deposition of GO Thin Films and TiO$_2$–GO Thin Films

GO thin films were fabricated by the vacuum filtration method [47,48]. GO (10 mg) was added to 300 mL of DI water and sonicated for 1 h. The GO suspension was then filtered through a mixed cellulose ester membrane (pore size: 0.22 µm). The GO film thickness could be varied by adjusting the filtration volume of the GO suspension. To optimize the film thickness, GO films were deposited using filtration volumes of 10, 15, 30, and 45 mL. Next, the film was transferred to the PET substrate and pressed for 12 h. The ester membrane was dissolved by soaking it in acetone for 1.5–2 h, rinsing it with methanol and DI water, and drying it in an oven at 40°C. To manufacture TiO$_2$–GO thin films, 10 mg of GO was dispersed in 200 mL of DI water and 100 mL ethanol. After sonication for 1 h, 5 mg of TiO$_2$ (P25, Degussa, London, UK) was added to the GO suspension. The TiO$_2$–GO suspension was sonicated for 1.5 h.

2.3. Graphene Patterning

GO and TiO$_2$–GO films were patterned using a pulsed light system that employed spectral wavelengths of 475–1200 nm. The apparatus providing the pulsed photon energy had five energy densities: 4.5, 5.0, 5.5, 6.0, and 6.5 J/cm$^2$. Figure 1 shows the pattern mask.
used in this study, which is a 5-inch mask with a Cr pattern deposited on quartz glass (thickness: 2.3 mm). The properties of the rGO thin films after reduction were examined by a four-point probe, AFM (Parker, Seoul, Korea), FE-SEM (JEOL, Tokyo, Japan), and Raman spectroscopy (Nanobase, Seoul, Korea).

Figure 1. Pattern mask design: line pattern and cube pattern.

3. Results and Discussion

Photo thermal reduction is a process in which GO is reduced to produce rGO due to the thermal energy of 300 °C or more, which is generated instantaneously as photon energy and is converted into thermal energy. According to Feng et al., as the layer thickness increases, the emissive thermal energy becomes smaller in 2D nanomaterial [49,50]. Meanwhile, thermal energy transfer depends on the thickness of GO films, which is controlled by the volume expansion of GO.

Hence, it is essential to determine the optimal volume of GO suspension required to form a GO thin film with a uniform thickness by the vacuum filtration method. In this method, the film thickness depends on the filtered GO solution. The thickness of GO thin film is analyzed by AFM after filtering 10, 15, 30, and 45 mL of a 0.033 mg mL$^{-1}$ GO solution (Figure 2). A linear relationship is observed between the GO film thickness and the volume of the GO suspension.

We have confirmed through previous experiments that a large amount of damage was caused by excessive thermal energy of a 0.2-μm-thick GO film. For instance, the experiment was performed with 0.45 μm films.

Figure 3 shows the patterned rGO-GO film resistance and optical image according to pulsed energy 6 J/cm$^2$ at one time. At an energy density of less than 30 J/cm$^2$, the reduction reaction does not even partially occur and the patterning is not successful, and it seems to be the most successful patterning when the energy density is 36 or 42 J/cm$^2$. Meanwhile, it has a similar resistance value. Therefore, Raman mapping was measured for a more accurate analysis (Figure 4).

Figure 4 shows the Raman spectroscopy mapping of a patterned rGO-GO film irradiated with 36 or 42 J/cm$^2$ energy density, which seems to be the most successful patterning in rGO sheet resistance and optical image.

Generally, carbon materials have a D band around 1350 cm$^{-1}$ and a G band around 1580 cm$^{-1}$ [51,52]. The D band is related to incomplete structural defects, and the G band is associated with E$_{2g}$ vibrational modes of sp$^2$ carbons.
Figure 2. Thicknesses of GO films obtained from various volumes of GO suspension.

Figure 3. The patterned rGO-GO sheet resistance and optical image according to pulsed energy 6 J/cm² at one time. Sheet resistance (a), optical images of 24 J/m² (b), 30 J/m² (c), 36 J/m² (d), and 42 J/m² (e).
According to Raman mapping, the GO film is partially reduced by pulsed energy, and it can be confirmed that the D band peak and the G band peak intensity of rGO and GO are different from each other. It is confirmed that the patterned rGO-GO film was efficiently reduced when the energy density of 42 J/cm² was irradiated (Figure 4b). Considering the sheet resistance result shown in Figure 3a, when the energy density of pulsed energy is irradiated at 36 J/cm², the thermal budget generated by pulsed energy is used to reduce GO, and the volume expansion of GO is small due to the relatively low thermal budget. On the other hand, it predicted efficiently reduced or rapid volume expansion of the GO film when the energy density of pulsed energy is 42 J/cm² compared to pulsed energy of 36 J/m². As a result, it has a thermal budget capable of an efficient reduction process without damaging the rGO line when pulsed energy is irradiated at 42 J/cm². Next, we show the result of the patterned rGO-GO film resistance and optical image according to pulsed energy 6.5 J/cm² at one time (Figure 5).

The GO reduction reaction does not occur partially when the total irradiated energy density is 6.5 J/cm², and rGO-GO film patterning is not successful. In comparison, it can be confirmed that the rGO-GO film patterning is relatively successful when the energy density of 19.5 J/cm². At an energy density of 26 J/cm², the damages appeared on the rGO line partially. Raman analysis performed each patterned rGO-GO film for precise analysis (Figure 6). In the optical image, the energy density of 19 J/cm² seems to be the most successful rGO-GO film patterning, and when the irradiation energy density is 26 J/cm², the rGO line seems to be defective due to an excessive thermal budget. Raman mapping results show the same results as expected in the optical image. When the energy density of 19 J/cm² was irradiated (Figure 6a), some damage of the rGO line was observed due to the volumetric expansion of GO. However, the film type maintained. Meanwhile, it can be confirmed that the defect on the rGO line when the energy density of 26 J/cm² was irradiated (Figure 6b) because of a decrease in adhesion to PET due to the rapid volume expansion of GO.

As a result, the damage-free rGO line is patterned by irradiating the energy density of 42 J/cm² when the pulse energy irradiated is 6 J/cm² can be demonstrated. However, it confirmed that the resistance of the rGO line is relatively high at 1.70 kΩ. On the other hand, the rGO line was most efficiently patterned by irradiating the energy density of 19 J/cm² when the pulse energy irradiated is 6.5 J/cm² because it has a low resistance of 1.10 kΩ.
Figure 5. The patterned rGO-GO sheet resistance and optical image according to pulsed energy 6.5 J/cm² at one time. Sheet resistance (a), optical images of 6.5 J/m² (b), 13 J/m² (c), 19.5 J/m² (d), and 26 J/m² (e).

The GO reduction reaction does not occur partially when the total irradiated energy density is 6.5 J/cm², and rGO-GO film patterning is not successful. In comparison, it can be confirmed that the rGO-GO film patterning is relatively successful when the energy density of 19.5 J/cm². At an energy density of 26 J/cm², the damages appeared on the rGO line partially. Raman analysis performed each pattered rGO-GO film for precise analysis (Figure 6). In the optical image, the energy density of 19 J/cm² seems to be the most successful rGO-GO film patterning, and when the irradiation energy density is 26 J/cm², the rGO line seems to be defective due to an excessive thermal budget. Raman mapping results show the same results as expected in the optical image. When the energy density of 19 J/cm² was irradiated (Figure 6a), some damage of the rGO line was observed due to the volumetric expansion of GO. However, the film type maintained. Meanwhile, it can be confirmed that the defect on the rGO line when the energy density of 26 J/cm² was irradiated (Figure 6b) because of a decrease in adhesion to PET due to the rapid volume expansion of GO.

Figure 6. Raman mapping of (a) energy density is 19 J/cm², (b) energy density is 26 J/cm² (300 × 300 µm²).

TiO₂ is the most commonly used photo catalysis due to its characteristics of photo catalysis performance, nontoxicity, easy availability, and long-term stability. TiO₂ were excited to generate electron–hole pairs under UV (~365 nm) irradiation. The holes reacted with surface-adsorbed water to generate oxygen and protons, and on the other hand, the electrons could be successfully captured by the sp² orbital of GO [49,50].
Figure 7 shows an FE-SEM image and Raman spectroscopy of the TiO$_2$-GO composite. Figure 7a shows the FE-SEM image of the TiO$_2$-GO composite. TiO$_2$ particles been formed on GO surface. Figure 7b shows the Raman spectrum of the TiO$_2$-GO composite. The Raman peaks observed at around 1350 cm$^{-1}$ and around 1580 cm$^{-1}$ can be assigned to the D band peak and G band peak, respectively. The D band is related to sp$^3$ defect and the G band is associated to the E$_{2g}$ of sp$^2$ C atom vibration mode of carbon. Furthermore, those observed at around 140 cm$^{-1}$, 400 cm$^{-1}$, 510 cm$^{-1}$, and 640 cm$^{-1}$ can be assigned to the E$_g$, B$_{1g}$, A$_{1g}$, and E$_g$, of the anatase phase, respectively.

Figure 7. (a) FE-SEM image and (b) Raman spectroscopy of TiO$_2$-GO composite.

Figure 8 shows the resistance and corresponding optical images of TiO$_2$-rGO films obtained using a pulsed photon energy of 5.5 J/m$^2$. When the energy density was below 16.5 J/m$^2$, no partial reduction reaction occurred, and patterning was not successful. The most successful patterning was obtained when the energy density was 22 J/m$^2$, as rGO-TiO$_2$ line defects were observed in the optical image when the energy density was 27.5 J/m$^2$. Notably, it indicated that the resistance increased as the irradiated energy density increased. Thus, it is considered that rGO-TiO$_2$ line defects affect the measured resistance in the four-point probe system [25].

The Raman mapping results (Figure 9) suggest that the GO films have been reduced through pulsed energy, and the intensity of the D band peak and the G band peak are displayed differently for TiO$_2$-rGO and TiO$_2$-GO. However, defects were generated in the TiO$_2$-rGO lines. In addition, unlike in the GO film, the edges of the rGO-TiO$_2$ lines in the TiO$_2$-GO are not linear. TiO$_2$-GO is instantaneously heated to 300 °C or more by the pulsed photon energy, and the generated thermal energy removes oxygen-containing functional groups from the GO surface. It is likely that defects occur in the rGO-TiO$_2$ lines owing to the difference in the thermal expansion coefficients of TiO$_2$ and GO, resulting in lines with nonlinear edges.

Figure 8. The patterned TiO$_2$-rGO sheet resistance and optical image according to pulsed energy 5.5 J/cm$^2$ at one time. Sheet resistance (a), optical images of 16.5 J/m$^2$ (b), 22.0 J/m$^2$ (c), and 27.5 J/m$^2$ (d).
The patterned TiO$_2$-rGO sheet resistance and optical image according to pulsed energy 5.5 J/cm$^2$ at one time. Sheet resistance (a), optical images of 16.5 J/m$^2$ (b), 22.0 J/m$^2$ (c), and 27.5 J/m$^2$ (d).

Figure 9. Raman mapping of energy density is 22 J/m$^2$: (a) $I_D$, (b) $I_G$, (c) $I_D + I_G$.

4. Conclusions

In this study, rGO-GO patterning by photothermal reduction and photocatalytic reduction was examined. rGO line damage on the irradiated GO films was influenced by the pulsed photon energy as well as the total irradiation energy density. Thus, to achieve damage-free rGO line patterning, the photon energy per pulse should be considered along with the total energy density. Damage-free rGO-GO patterns were obtained by irradiating a thin GO film (thickness: 0.45 μm) using a photon energy of 6.0 J/m$^2$ per pulse with an energy density of 42 J/m$^2$ or a photon energy of 6.5 J/m$^2$ per pulse with an energy density of 26 J/m$^2$. Otherwise, it was determined that when the pulsed photon energy
was irradiated at one pulse lower than the GO film, the reduction reaction of TiO$_2$-GO happened. However, the TiO$_2$-GO system exhibits inconsistencies owing to differences between the thermal expansion coefficients of TiO$_2$ and GO.

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