Polymers. Additionally, these patterning methods have shown narrow width, low coverage on large area substrates, and residual serious contamination of the graphene. Therefore, the reduction of surface contamination and damage on the transferred graphene is an important issue and the development of an in-situ transfer method would be beneficial for a variety of device applications.

The conventional transfer process essentially involves the transfer of chemical vapor deposition (CVD)-grown graphene onto the target substrate after dissolving the catalytic metal. This conventional transfer process requires special care to avoid formation of damages such as wrinkles and bubbles in transferred graphene layer. It was reported that the presence of wrinkles and bubbles on the graphene reduces the conductance of graphene. Additionally, polymer materials, which are generally used as a graphene-supporting layer to prevent folding or tearing of the graphene during the metal-etching step, cause serious contamination of the graphene. Therefore, the reduction of surface contamination and damage on the transferred graphene is an important issue and the development of an in-situ transfer method of high-quality graphene would be beneficial for a variety of device applications. Here, we report the in-situ transfer method of patterned graphene in solution by using patterned supporting layers. The in-situ transfer method of graphene can find application where high-quality and large-scale patterned graphene is required without any damage to the graphene during the transfer process. The graphene with excellent properties, such as large area, low resistivity, high carrier mobility, and high transparency at broad spectral region, could be used as a transparent electrode material for use in electronic devices, memory devices, circuits, transistors, and solar cells. The patterning of graphene has been very important factor for the diverse device applications. The patterning methods of graphene include the elastomer stamp method, laser cutting method, direct inkjet printing, and self-assembled template-assisted method. However, such methods have suffered from the formation of patterned graphene with narrow width, low coverage on large area substrates, and residual polymers. Additionally, these patterning methods have shown some limitations on the transfer of high-quality graphene, as the graphene should be transferred from the catalytic metal to the target substrate.

We report the selective growth and in-situ transfer of graphene on a gallium nitride layer in solution using patterned SiO2 supporting layers. The line-patterned multilayer graphene was selectively transferred onto a gallium nitride target substrate without producing the damage and defect in the graphene. Furthermore, the transfer yield of in-situ transferred graphene was greatly increased compared to that by the conventional transfer method and the adhesion of transferred graphene was also improved by in-situ transfer in solution.

Experimental

Figure 1 provides a schematic of the selective growth of graphene and the in-situ transfer method. GaN grown on a sapphire substrate, which is widely used in the area of optoelectronics, was used as a target layer for the in-situ transfer of graphene. A 300-nm-thick SiO2 layer was deposited on a GaN layer as a supporting layer for the selective growth of graphene by plasma-enhanced CVD. As shown in Fig. 1a, the line-shaped SiO2 layers were fabricated by using the line-shaped photoresist (PR) mask with a width of 5 μm and a buffered oxide etchant. Prior to the planar deposition of the Ni layer, the PR was spin coated again on the line-patterned SiO2 layer to fill the empty space between SiO2 patterned lines as shown in Fig. 1b. After a 100-nm-thick Ni film was deposited by using electron-beam evaporation, the PR was removed to create voids between the SiO2 patterned lines. Multilayer graphene (MLG) was selectively grown at the bottom of the Ni layer in the CVD system with a flow rate of 10 sccm of CH4 gas, 20 sccm of H2 gas, and 480 sccm of Ar gas at 1000°C for 2 min. After the CVD growth of graphene, SiO2 supporting lines and Ni catalysts were removed by the buffered oxide etchant and iron chloride solution (FeCl3), respectively. After the SiO2 patterned lines and Ni catalysts were removed in sequence, the line-patterned graphene films were directly transferred onto the GaN substrates in the solution, as shown in Fig. 1f.

Results and Discussion

Figure 2a shows the scanning electron microscopy (SEM) image of the voids that were produced for graphene growth after the PR was removed. The void was used as a space for the transport of gases for the selective growth of graphene at the bottom side of the Ni layer. The formation of void was affected by the thickness of SiO2. It was difficult to form the void at the thickness of SiO2 below 100 nm. At the thickness above 400 nm, it was also difficult to transfer the graphene because the patterned graphene was easily detached from GaN layer during Ni etching process. Therefore, the SiO2 layer with an optimal thickness of 300 nm was used to form the void between GaN and Ni layer. It was reported that the hydrocarbon molecules decompose at the Ni surface and carbon atoms diffuse into the Ni layer at high temperature during the growth of the graphene on the Ni. Therefore, we optimized the amount and flow time of CH4 gas to selectively grow a graphene at the bottom of the Ni layer by keeping a high concentration of carbon atoms for sufficient diffusion into the Ni layer. Graphene was then segregated and synthesized on the bottom surface of the Ni layer through rapid cooling to room temperature by the flowing of Ar gas.

Figure 3a shows the Raman spectra of line-patterned graphene. To compare the properties of transferred graphene, we prepared another GaN sample with patterned graphene fabricated by using a conventional patterning process including reactive-ion etching (RIE). To obtain bare graphene from the Ni layer, poly(methyl...
methacrylate) (PMMMA) was used as a graphene-supporting material for FeCl₃ wet etching of the Ni layer. The patterned PR layer was used as an etching mask for line-patterned graphene. The insets in Fig. 3a present the optical microscope (OM) images and clearly show the arrays of patterned graphene layers transferred onto the GaN by using the in-situ direct transfer (top of Fig. 3a) and the conventional transfer methods (bottom of Fig. 3a). The arrows indicate the regions of graphene where the Raman spectra were measured. The Raman spectra show two distinct peaks, the G peak at 1580 cm⁻¹ and the 2D peak at 2700 cm⁻¹, which are typical features of graphene. The intensity of the G peak is stronger than the 2D peak, which is a feature of MLG. However, the intensity of the D peak near 1350 cm⁻¹, which is indicative of the presence of defects in the graphene layer, is greater for the graphene patterned by conventional transfer than that observed for the graphene patterned by in-situ transfer, as shown at the top of Fig. 3a. The weak D peak intensity of graphene patterned by in-situ transfer indicates that the formation of additional defects such as small cracks, wrinkles, and other imperfections created by the conventional transfer process is suppressed by the in-situ transfer of graphene in solution. Additionally, the in-situ transfer method can prevent contamination from supporting polymer materials such as PMMA, poly(dimethylsiloxane), or thermal release tapes, which are generally used for assisting graphene transfer. Therefore, this in-situ transfer method makes it possible to produce a clean graphene surface without any residue originating from the polymer supporting materials.

We measured the current-voltage (I-V) characteristics of graphene to investigate the electrical properties of the transferred MLG. The
100-nm-thick Au layers were deposited on the patterned graphene/semi-insulating GaN. Figure 3b shows I-V curves of the graphene layer patterned by the in-situ and conventional transfer methods. The I-V curves of both samples indicate that the line-patterned graphene layers are electrically conducting. The sheet resistance is estimated by $R_s = (R \times w)/L$, where $R$ is the resistance which is derived from 1/slope of the I-V curves, $w$ is the width of the graphene, and $L$ is the length of the graphene. Table I shows that the sheet resistance of patterned MLGs is estimated to be $300 - 1000 \ \text{Ω/sq}$, respectively. Considering that the CVD-grown graphene usually has a sheet resistance of $300 - 1000 \ \text{Ω/sq}$, the sheet resistances of both samples are in the typical range of sheet resistance of graphene grown by CVD.30,31

The transfer yield of graphene patterned by the in-situ and conventional transfer methods was investigated by counting the number of electrically conducting lines of patterned graphene. Figure 4a and 4b show the OM images of transferred graphene after the lift-off process for metal electrodes. Figure 4a shows that graphene patterned by the in-situ transfer method is not damaged or detached from the GaN layer during the pattern transfer of graphene. However, as shown at the top of Fig. 4b, disconnected lines of graphene are observed after the numerous steps of the conventional transfer process. During the metal lift-off process for the formation of contact electrodes, the graphene layer patterned by the conventional transfer method was torn out or etched away with the metal because the patterned graphene is very fragile owing to the thin thickness and narrow width of graphene, as shown in Fig. 4b. The poor interfacial adhesion between the graphene and GaN layer also limits the use of graphene in diverse device applications because the graphene is easily detached during the device fabrication processes.31,32 Figure 4c shows the transfer yield of graphene layers patterned by in-situ and conventional transfer methods as a function of distance between the two Au contact electrodes in the geometry shown in the inset of Fig. 3b. The transfer yield was estimated by counting the number of perfect line-patterned graphene, which was about 80 line patterns. The transfer yield is decreased with increasing the distance between contact electrodes. At a distance of 30 μm, most of the graphene layers patterned by the in-situ and conventional transfer methods adhere well to a GaN layer. However, the transfer yield of graphene layers patterned by conventional transfer method is dramatically reduced from 90 to 45% as the distance increases from 30 to 430 μm, whereas that of graphene layers produced by the in-situ transfer method is almost independent of the distance. These results show that the line-patterned graphene by in-situ transfer has stronger adhesion than line-patterned graphene by conventional transfer because the in-situ transfer method is less affected by the external environment. It is suggested that the graphene patterned by the conventional transfer method has poor adhesion because the residue at the interface such as an oxide layer, polymer, air bubble, or water droplet, remain on the graphene layer during the conventional patterning process. In the case of the in-situ transfer method, however, the trapping of interfacial residuals, water droplets, or air bubbles can be minimized because the process solution such as FeCl₃, air, and water, can be easily removed from the patterned graphenes in the solution. Therefore, the adhesion of the graphene can be greatly improved by the in-situ transfer method.

Our approaches for selective growth and in-situ transfer of graphene might be readily applied to other substrates. The PECVD, photolithography, and etching processes employed in this study have been conventionally used in the Si-based device processing. It was also reported that the growth temperature for graphene could be reduced to 300 °C by using liquid carbon sources in metal-catalytic CVD growth method.33 Furthermore, most substrates including SiO₂, Si₃N₄, and Si are chemically stable in the aqueous FeCl₃ solution used for Ni etching. Therefore, it is expected that these methods can be applied to produce the nanoscale and single layer graphene by using nano-patterning and catalytic CVD growth using copper.

Conclusions

In conclusion, we have demonstrated a facile transfer method by showing high quality patterned MLGs can be successfully transferred on GaN substrates in solution. The in-situ transfer method improves the adhesion of the graphene on the substrates and the transfer yield of graphene is more than 90%. Our approach can be used as a promising transfer technique for various graphene-based devices.

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### Table I. Resistance and estimated sheet resistance of the graphene layer patterned by the in-situ and conventional transfer methods.

<table>
<thead>
<tr>
<th>Width (W)</th>
<th>Length (L)</th>
<th>$R$ (1/slope)</th>
<th>Estimated sheet resistance ($R_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DG</td>
<td>5.4 μm</td>
<td>60 μm</td>
<td>6.02 kΩ</td>
</tr>
<tr>
<td>CG</td>
<td>4.7 μm</td>
<td>60 μm</td>
<td>5.35 kΩ</td>
</tr>
</tbody>
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References