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Site-selective Deposition of Graphene Oxide Layer on Patterned Self-assembled Monolayer

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Patterned graphene oxide (GO) layer is prepared by site-selective deposition of GO on patterned self-assembled monolayer (SAM). Deep ultraviolet (DUV) exposure on octadecyltrichlorosilane (OTS) SAM through photomask produces hydrophobic/hydrophilic pattern, and the hydrophilic region is reacted with aminopropyltriethoxysilane (APTES), which is preferentially wetted with GO through ionic interaction between carboxylic acid groups of GO and amino groups of APTES SAM. As-prepared GO pattern can be further transformed to chemically reduced graphene oxide (RGO) pattern after chemical reduction with hydrazine. Both Raman and electrical conductivity measurements confirm the successive preparation of RGO pattern.

Graphene, a single-atomic layer of fully conjugated sp^2-carbons has been extensively researched due to its fascinating electrical, mechanical, and thermal properties owing to its unique two-dimensional (2D) structure.[1] Mechanical cleavage, chemical vapor deposition (CVD), and wet process by using either GO or RGO have been attempted for utilizing graphene-based materials in various device platforms.[2] Among these, wet processes have several advantages compared with others because large-area device fabrication of graphene can be accomplished through various solution processes such as ink-jet printing and soft lithography.[3] Photolithography is a practical patterning method in the semiconductor industry. Recently, formation of patterned graphene layer by photoresist-masked etching through photolithography has been demonstrated.[4] Both solubility of GO in water and its hydrophilicity prompt us to develop a new patterning strategy using patterned self-assembled monolayer (SAM) through photolithographic technique. DUV exposure on SAM-modified silicone (Si) wafer or polymer film through photomask has been known to produce hydrophilic/hydrophobic patterns on SAM.[5] Therefore, preferential wetting of hydrophilic GO above a hydrophilic patterned area can result in patterned GO layer either on Si wafer or polymer film. In this study, patterned RGO film is prepared through photolithography using SAM resist, site-selective deposition of GO, and chemical reduction by using hydrazine vapor.

Either OTS-modified Si wafer or polystyrene (PS) film can be used as either a hard or flexible substrate. OTS-modified Si wafer can be prepared by simple dipping of Si wafer having thermally grown oxide layer (ca. 300 nm) into anhydrous toluene solution of OTS (0.1 M), producing uniform OTS SAM. Overall SAM formation must be done under strictly anhydrous conditions because self-crosslinking of OTS molecules in the presence of water might produce certain aggregated structure in OTS SAM.[6] The water-droplet contact angle on OTS-modified Si wafer is 102° because hydrophobic octadecyl groups are covalently linked on the Si wafer. DUV exposure of this hydrophobic OTS SAM clearly provides hydrophilic region. Water-droplet contact angle changes from 102 to 12° within 6 min (Figure 1a). PS film also shows decrease of water-droplet contact angle, but this process is slower than OTS-modified Si wafer. DUV exposure with wavelength of 184.9 nm using a low-pressure mercury lamp (28 mW cm^{-2} of intensity from 6 mm distance at 25 °C at 1 atmospheric pressure) for 10 min is required to decrease original contact angle of PS film (56°) to 15° (Figure 1b). This faster response of OTS-modified Si wafer compared with PS film is believed to originate from the monolayer thickness of OTS SAM and lower reactivity of styrenic moieties of PS for the photooxidation reaction by DUV exposure.

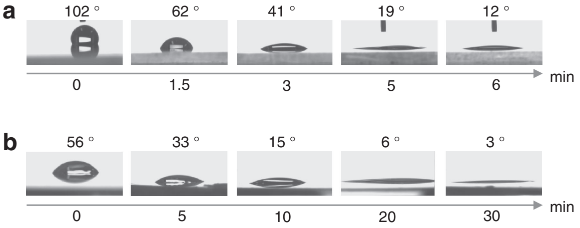

Figure 1. Pictures of water droplets and contact angles after DUV exposure on a) OTS-modified Si wafer and b) PS film.

The successful transition from hydrophobic state to hydrophilic state of either OTS-modified SAM or PS film prompted us to prepare patterned GO or RGO layer on them. The adhesion between hydrophilic GO having carboxylic acid groups and DUV-exposed hydrophilic area can be enhanced by the modification of hydrophilic region by reaction with APTES.[7] In this case, N-terminal groups of APTES region can interact with carboxylic acid groups of GO through ionic interaction after acid–base reaction. The overall procedure for the preparation of patterned RGO film on OTS-modified SAM is presented in Figure 2. At first, hydrophobic–hydrophilic OTS pattern is developed through DUV exposure for 12 min through photomask. Then, the substrate is dipped in toluene solution of APTES, resulting in OTS/APTES pattern.[8] Then, GO solution with 1 mg of GO in 1 mL of deionized water is dip-coated on as-prepared OTS/APTES pattern, resulting in patterned GO layer. Deposition of GO plates on hydrophilic APTES region is clearly observable due to the different color of GO-coated region (Figure 3a). This deposition of GO is site-selective because ionic interaction between GO plates and amino groups of APTES is possible only in APTES-coated region. The thickness of deposited GO layer could be easily controlled by repeating of the dip-coating process. Facile layer-by-layer deposition of GO plates on preformed GO layer is likely through hydrogen bonds between protonated carboxylic acid or hydroxy groups of neighboring GO plates because the pH of used GO solution is

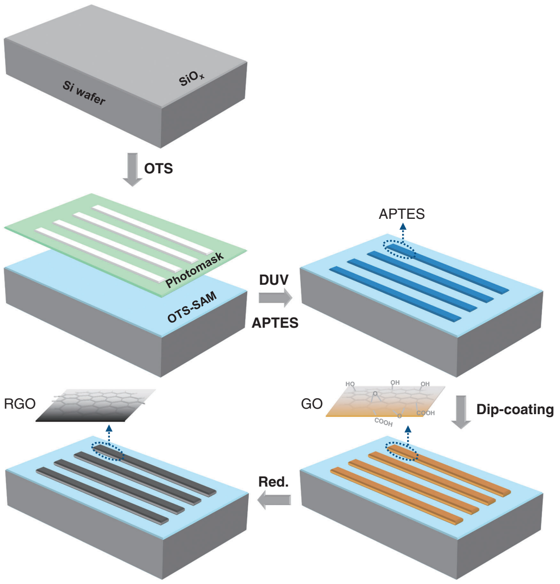

Figure 2. Schematic illustration of the preparation process of GO and subsequent RGO patterning on OTS-SAM-modified Si wafer.

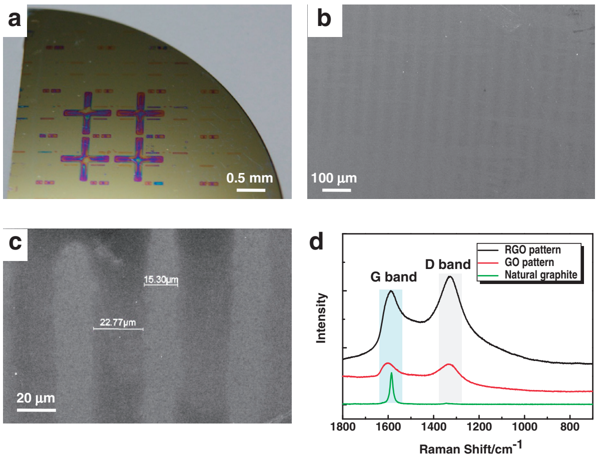

Figure 3. a) Photo image of pattered GO layers through dip-coating with GO solution (the purple colored region is GO-coated region and yellow backgroud is thermally grown oxide layer), b) and c) SEM images of line patterned GO layer (the bright region is GO layer and dark background is OTS SAM), and d) Raman spectra of prepared RGO pattern, GO pattern, and natural graphite.

around 6, where protonation of carboxylic acid groups is more prevailing than deprotonation.

This dip-coating procedure requires precise control of withdrawal speed, viscosity, and solvent polarity.[9] From the fact that both dynamic light scattering (DLS) and atomic force microscopy (AFM) show broad size distribution centered around 0.8 µm, it is evident that fabrication of nanometer-scale graphene pattern requires much more consideration because the large size of GO plates might result in large line edge roughness. GO line pattern around 20-µm width shows that the line edge structure is not flat and uniform in SEM image (Figures 3b and 3c). Decreasing of line edge roughness might be another challenging task for the fabrication of graphene-based devices in submicrometer scale through wet process. Patterned GO layer was also formulated on hydrophobic/hydrophilic pattern from PS film, but the pattern quality is not good probably due to lower hydrophobicity of PS layer compared with OTS SAM. Roughness of PS film compared with OTS monolayer might contribute nonpreferential wetting of GO even on hydrophobic regions in this case.

Reduction of GO pattern to RGO pattern is further examined by Raman analysis of both patterned layers. RGO pattern shows both G and D bands at 1587 and 1328 cm^{-1} and shows increased D band to G band intensity ratio of 1.21 (I(D)/I(G)) compared with 1.04 of GO (Figure 3d). These are typical features of Raman spectra of RGO obtained by chemical reduction from GO.[10] Then, the electric conductivity of RGO layer was examined. The thickness of RGO layer can be easily controlled by repeated dip-coating of GO solution. Sheet resistance of $4 \times 10^5\ \Omega$/square of 100-nm thick patterned RGO layer which is obtained by dip-coating is comparable to RGO film which is prepared by filtration of GO solution, confirming that molecular packing of graphene plates through dip-coating is similar with the densely packed structures of filtered RGO film.

In summary, GO pattern was prepared by site-selective deposition of GO on patterned SAM which is obtained by patterned DUV exposure on OTS SAM and further reaction with APTES. Hydrophilic GO is preferentially wetting on hydrophilic APTES region through electrostatic interaction between carboxylic acid groups of GO and amino groups of APTES SAM. While this directed deposition method can produce clear GO pattern or RGO pattern in micrometer scale, line edge structure is not as uniform as conventional photoresist pattern from photolithography.

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