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Fabrication of Reduced Graphene Oxide Micro Patterns by Vacuum-ultraviolet Irradiation: from Chemical and Structural Evolution to Improving Patterning Precision by Light Collimation

As an oxygen-decorated derivative and a widely-studied precursor of graphene, graphene oxide (GO) has distinctive characteristics compared to graphene. The most important advantage of GO and its corresponding reduced material, reduced graphene oxide (rGO), is that easy mass-production is already available.[1] Compared with the commonly utilized thermal and chemical reduction of GO, the photoreduction processes demonstrate their special advantages, *e.g.*, higher efficiency, precise control of the oxygen-containing functional groups, feasibility of fabricating rGO micro-patterns along with reduction, less energy consumption and non-release of toxic pollutants.[2] Practical UV and VUV light sources are expected to be good candidates for fabricating the micro-scaled GO and rGO patterns on solid-state substrates.[3] Our group has demonstrated a VUV reductive patterning method which adopted a quartz photomask to define the GO and rGO periodic patterns. [4–6] However, there were still critical questions concerning the photoreduction mechanism, unintended low electrical conductivity and inevitable mismatch of patterns after long-time irradiation. Although the total UV exposure dose of *ca.* 480 J·cm^{-2} was much higher than the VUV exposure dose of *ca.* 40 J·cm^{-2} that we previously reported, the final oxygen / carbon atomic ratios ($R_{O/C}$) reached a similar value at 0.25~0.29.[3,6] That raised a question on what is the original difference between UV and VUV reduction of GO. Besides, the previously reported VUV photoreductive patterning of GO achieved in fabricating 5 µm wide rGO lines at 10 µm. However, it shows apparent patterning mismatch between photomask and fabricated patterns when increasing the exposure time (Figure 1a, b), which resulted in an insufficient reduction of GO and a consequent low electrical conductivity. Here, we report a study of VUV reduced GO in high vacuum by using X-ray photoelectron spectroscopy (XPS) and Kelvin probe force microscopy (KFM), which provide a deep understanding of the mechanism of VUV photochemical reduction of GO and its difference from UV reduction. Based on the elemental analysis results, the photochemical reactions were clarified. The higher reduction efficiency of VUV reduction than UV reduction was explained. That was ascribed to the difference in photocatalytic and photochemical process caused by the photon energy difference. KFM demonstrated the local variation of surface potential during reduction, which revealed that the VUV reduction did not homogeneously progress in GO. By using conductive atomic force microscopy (CAFM), the improvements in conductivity of the rGO bilayer and in-planar structure of rGO were studied.[7] By measuring the conductivity of the bi-layered rGO, the electrical conductivity was estimated to be in the order of 10^0 ~ 10^2 S · m^{-1}, which can be used as an organic semiconductor. The origin of the VUV photopatterning mismatch was clarified to be the tilted incident light. A hollow column was used to semi-collimate the VUV light, which effectively reduced the mismatch (Figure 1d~f). Compared to the pattern in Figure 1b, same-sized rGO pattern without obvious mismatch was successfully drew onto GO (Figure 1c). As shown in Figure 1g, the highest pattern resolution of rGO was 1 µm at 4 µm intervals. CAFM current mapping (Figure 1h, i) verified the conductive difference between GO and rGO. This photochemical reduction strategy needs no chemicals, performs at ambient temperature and is satisfactory for industrial cost-effectiveness. The resist-free patterning shows no restriction on substrate materials because VUV light is thermally and chemically nondestructive except for photochemical degradation of some polymer substrates. We hope that this method will become a fundamental technique for fabricating rGO-based micro devices.

References

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Figures

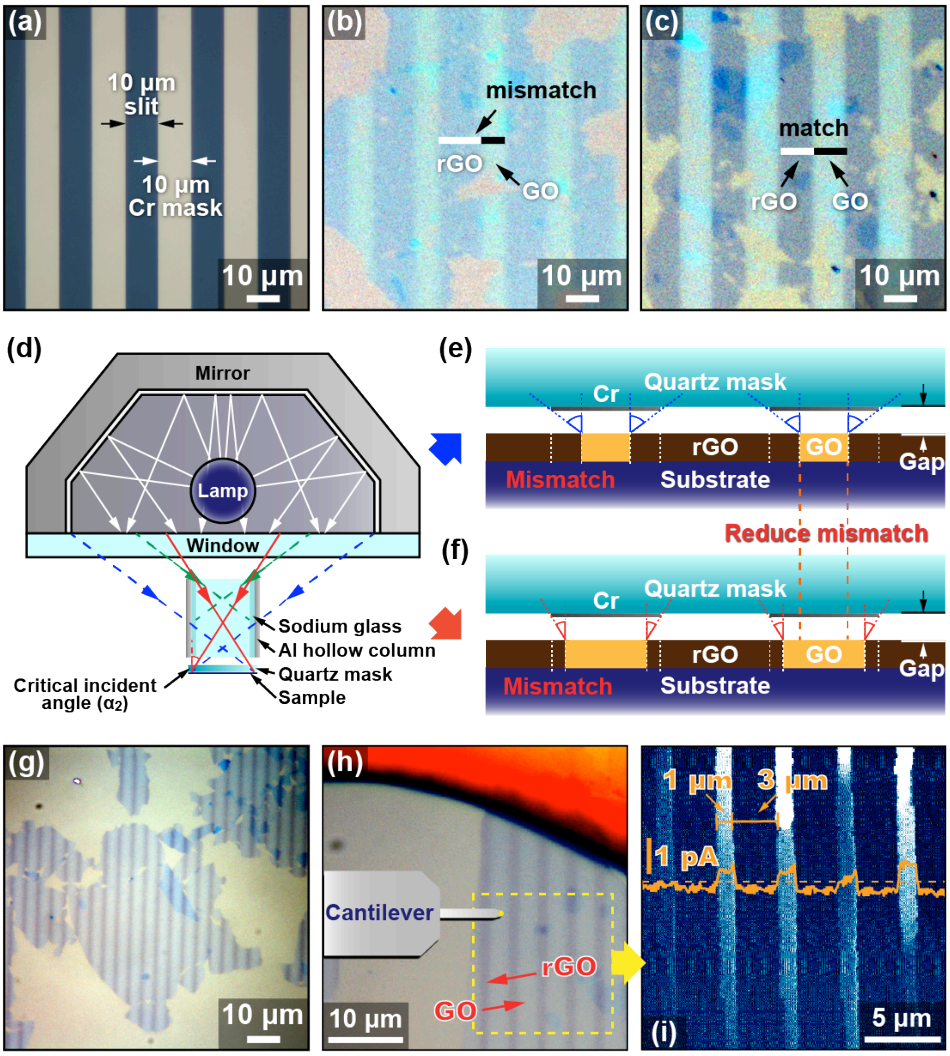

Figure 1: Reduction of patterning mismatch by collimating the VUV light. (a) Microscopic image of the photomask. The golden lines are the Cr masks which are periodic 10 μm lines at 20 μm intervals. (b, c) 10 μm rGO line pattern at 20 μm intervals which was fabricated (b) without and (c) with collimating the VUV light. The inset white bar and black bar in panel b and c represent the width of rGO lines and GO lines, respectively. (d) Schematic illustration of the modified VUV photoreduction system. The VUV light would be reflected by the Al mirror and be angled to irradiate the sample. By using the hollow column, the blue dashed incident light would be blocked by the Al foil while the green dashed light would be absorbed by the sodium glass. The critical incident light with the largest incident angle would be the red light. (e, f) The magnified schematic illustration at the photomask-substrate interface showed how deep the tilted incident light can penetrate (e) without and (f) with the hollow column. (g) Fine rGO/GO patterns fabricated by using collimated VUV light of 1 μm rGO line pattern at 4 μm intervals. (h) CAFM measurement. (h) CAFM current mapping image corresponding to panel b. The insets show the corresponding current profiles.