Fe-catalyzed Etching of Graphene and Few-layer Graphene

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Fe-catalyzed etching of graphite and few-layer graphene (FLG) has been used to create channels with desired crystalline edges [1,2]. Due to the strong Fe-C interaction, graphene can be etched through either carbon hydrogenation or carbon dissolution into Fe alone. In this work, we investigated the Fe-catalyzed etching of graphene and few-layer graphene (FLG) in forming gas (10% H_2/90% N_2) or N_2. Fe thin films were deposited onto mechanically exfoliated graphene and FLG flakes on Si/SiO_2 substrates using a sputtering technique. When the thin film was rapidly annealed in either gas environment, particles were produced due to the dewetting of the films [3], and etching of graphene and FLG occurred. Low-voltage scanning electron microscopy (LVSEM) and Raman spectroscopy have been used to characterize the etched graphene and FLG regions. The combined microscopic and spectroscopic evidence reveals the strikingly different carbon residues in etched graphene and FLG regions produced in these two different gas environments, thus providing an insight into the catalytic mechanisms.

Figure 1a shows an optical image of mechanically exfoliated graphene and FLG regions on a Si/SiO_2 substrate before depositing a Fe thin film. Figures 1b-1c show the representative Raman spectra of pristine graphene and FLG collected around G and Gˈ peaks, respectively. As the number of graphene layers (N) increases, the intensity of G peak increases (Figure 1b). Figure 1c shows the change of Gˈ peak in position, shape, and intensity as the number of graphene layers graphene changes. The exact numbers of the graphene layers ranging from 1 to 7 (1L to 7L labeled in Figure 1a) are determined by the fact that the integrated area of G peak increase almost linearly as the number of graphene layers increases. After annealing the Fe thin film at 950 ^{o}C for 30s in a forming gas environment, the LVSEM image (Figure 1d) of the area in Figure 1a reveals that the dewetting of the Fe thin film takes place and the particles have been produced in the graphene, FLG, and substrate regions. The particles in the 1L, 2L, and 3L graphene regions are more densely distributed than those in the 6L and 7L graphene regions. The Raman spectra (Figure 1e) collected from the post-annealing graphene and FLG regions change significantly from those from their pristine counterparts. For monolayer graphene, after annealing the Fe thin film, a peak ~1350 cm^{-1} (the D peak) appears and both the G and G' peaks are significantly attenuated and broadened. The appearance of the D peak in the spectrum collected from the post-annealing graphene region, together with the significant reduction in the intensity of G and G' peaks, suggests that the graphene is severely etched but that there exists sp^2 carbon in the etched graphene region. For the spectrum collected from post-annealing bilayer graphene region, D and G peaks are also clearly observed. Interestingly, for the spectra collected from the post-annealing 3L to 7L graphene regions, no D, G, and Gˈ peaks are observed. However, we notice that all the Raman spectra collected from the post-annealing graphene and FLG regions exhibit an upward-sloping photoluminescence (PL) background. As the number of graphene layers increases, the PL slope increases.

Etched graphene and FLG were also observed for the Fe film annealed in N_2, suggesting that this graphene etching process can also occur through a carbon diffusion process. However, the Raman spectra collected from post-annealing graphene and FLG regions in N_2 still exhibit strong Raman G and G' peaks even with the presence of the D peak and no up-sloping PL background. LVSEM images reveal the visible graphene and FLG residues among the particles. We attribute the strong PL background from the carbon residues in the etched graphene and FLG regions produced in forming gas to the formation of hydrogenated amorphous carbon [4]. Therefore, our results provide insights into the catalytic roles which Fe particles play during the carbon hydrogenation in the dissociation of hydrogen into hydrogen atoms and in the production of hydrogenated amorphous carbon.

References

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Figures

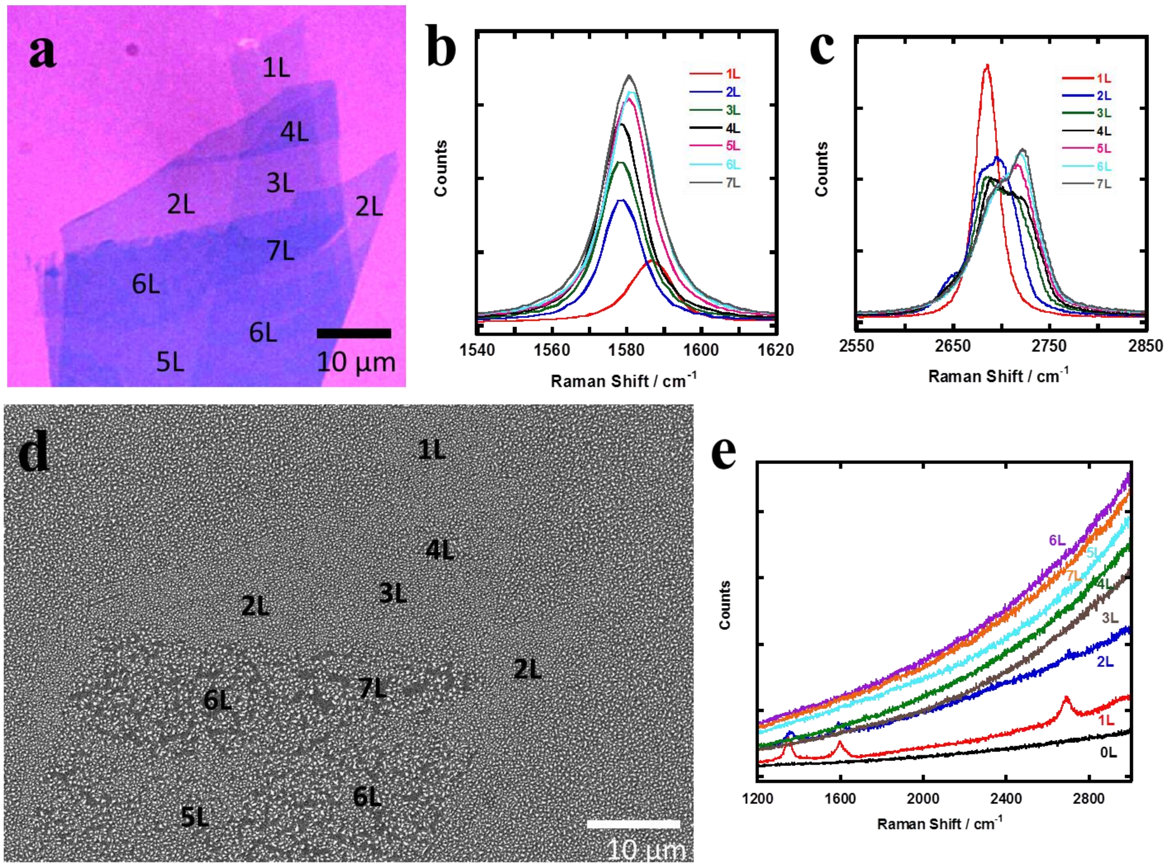

Figure 1. (a) Optical images of pristine graphene and few-layer graphene (FLG) on a Si/SiO2 substrate. (b,c) Representative micro-Raman spectra of graphene and FLG in the regions of G and G' peaks, respectively. (d) LVSEM image of post-annealing graphene and FLG regions in forming gas. (e) Representative micro-Raman spectra collected from post-annealing graphene and FLG regions in forming gas.