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Nitrogenation of monolayer graphene films in N_2 and N_2-O_2 flowing afterglows: analysis of incorporation-limiting mechanisms

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Abstract content

Monolayer graphene films are exposed to the flowing afterglow of a low-pressure microwave nitrogen plasma, characterized by the absence of ion irradiation and significant populations of N atoms and N2(A) metastables. Hyperspectral Raman imaging of graphene domains reveals damage generation with a progressive rise of the D/G and D/2D band ratios following subsequent plasma treatments. Plasma-induced damage is mostly zero-dimensional and the graphene state remains in the pre-amorphous regime. Over the range of experimental conditions investigated, damage formation increases with the fluence of energy provided by heterogenous surface recombination of N atoms and deexcitation of N2(A) metastable species. In such conditions, X-ray photoelectron spectroscopy reveals that the nitrogen incorporation (either as pyridine, pyrrole, or quaternary moieties) does not simply increase with the fluence of plasma-generated N atoms but is also linked to the damage generation. Based on these findings, a surface reaction model for monolayer graphene nitrogenation is proposed. It is shown that the nitrogen incorporation is first limited by the plasma-induced formation of defect sites at low damage and then by the adsorption of nitrogen atoms at high damage. Inspired by these findings, experiments were also realized in presence of oxygen impurities in the flowing afterglow. Over the range of experimental conditions investigated, the extent of damage observed by Raman is much more pronounced in the presence of oxygen. However, similar damage progression curve is observed in all cases : damage formation again increases with the fluence of energy provided by heterogenous surface recombination of N atoms. Hence, additional damage mostly results from a rise in the population of N atoms in N_2+O_2 and not to any specific role of oxygen in the plasma-graphene interaction. For comparable plasma-induced disorder levels, much lower nitrogen incorporation is observed by XPS in presence of oxygen impurities. In such conditions, nitrogen incorporation seems to compete with a surface recombination process leading to the production of NO, and therefore to a nitrogen loss. These aspects of competition between the various surface processes have been observed previously for the treatment of wooden materials in the same type of plasmas.

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