ICMTF 2019

19-24 May 2019

Symposium F: New Horizons in Coatings and Thin Films
Session F3: 2D Materials: Synthesis, Characterization, and Applications

Mechanism of formation of nitrogenated doped graphene films, investigated by in situ XPS during thermal annealing in vacuum

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The introduction of dopants, such as nitrogen, into the graphene network, is paramount for many applications such as nanoelectronics, nanophotonics, sensor devices and green energy technology. One way consists in thermal heating of a doped solid carbon source, such as an amorphous a-C:N film, in the presence of a metal catalyst, to obtain nitrogenated graphene (NG) layers. The control of such a process requires to investigate diffusion and segregation mechanisms of the graphene precursor through the metal catalyst.

In the present study, the mechanism of atomic diffusion and NG film growth through a nickel catalyst thin film was investigated using in situ X-ray photoelectron spectroscopy (XPS) performed during thermal heating responsible for NG synthesis. Amorphous a-C:N films, containing 16%at. nitrogen, 10 nm thick, were synthetized by femtosecond pulsed laser ablation on fused silica substrates. A 150 nm thick nickel film was subsequently deposited by thermal evaporation on the a-C:N films. Thermal annealing at various temperatures (200, 300, 500 and 650°C), with different time durations, were performed in ultra-high vacuum during *in situ* XPS analysis, to carry out the top surface genesis of the NG film onto the nickel catalyst. FEG-SEM, Raman and X-ray absorption (XAS) spectroscopies were also performed to elucidate the nature and chemical composition of NG films. The diffusion of carbon and nitrogen through the nickel film towards the surface from 300°C was observed, without any graphene signature. Graphene films are formed at the highest temperatures, with a final 3%at. nitrogen content, in both pyrrolic and pyridinic configurations. In addition, the kinetics of carbon surface enrichment observed using in-situ XPS is discussed in the frame of the interface segregation theory and modelled using the du Plessis approach. The solid-state transformation mechanism responsible for the formation of few-layer NG films is thus investigated.

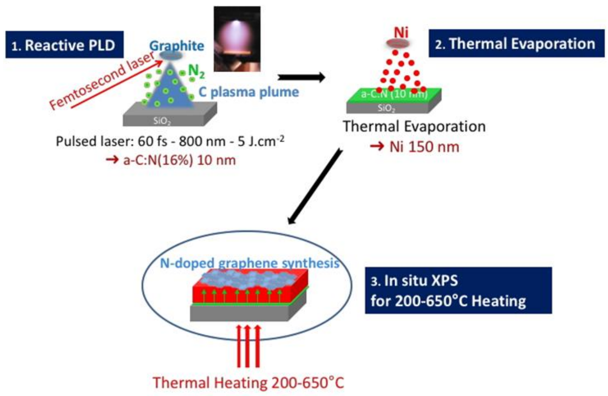

Figure: Synthesis process of N-doped Graphene films, by thermal heating of a Ni/a-C:N(16at.%)/SiO2 with in situ XPS analysis.