Combining nitrogen doping and vacancies for tunable resonant states in graphite

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Defect engineering in 2D materials is a promising approach for properties enhancement relevant for technological applications. In this context point defects such as nitrogen doping and vacancies have focused a lot of attention on graphitic materials such as graphene and graphite.
Nitrogen doping enhances and tunes graphene properties potentially extending its application possibilities compared to the pristine form. Nitrogen leads to a n-doping together with the formation of a resonant unoccupied state [1]. The other way of structural manipulation of graphene is a controlled vacancy creation. This technique has been demonstrated to tune graphene or graphite properties through the formation of a resonant electronic state [2].
Here we have combined Ar ion sputtering with remote nitrogen doping in a graphite sample in order to first investigate the Ar+ irradiation effects by probing the created vacancies and characterizing their electronic signatures. We also investigate how the nitrogen doping influences the electronic properties at the vacancy sites. First of all, we find that the nitrogen doping in graphite is acting very siùilarly to what has been reported in graphene. Secondly, we observed using scanning tunneling microscopy/ spectroscopy STM/STS the formation of different types of vacancies. Our spectroscopic study reveals the formation of peaks in the density of states in the unoccupied state region for vacancies in pristine graphite, while after nitrogen doping the peaks turn to the occupied states region. This allows to envision new strategies to tune the activity of graphite by controlling different types of active sites with potentially a donor or acceptor character.

[1] F. Joucken et al., Phys. Rev. Materials 3, 110301 (2019)
[2] E. H. Ahlgren et al., Phys. Rev. B 88, 155419 (2013)

Figures

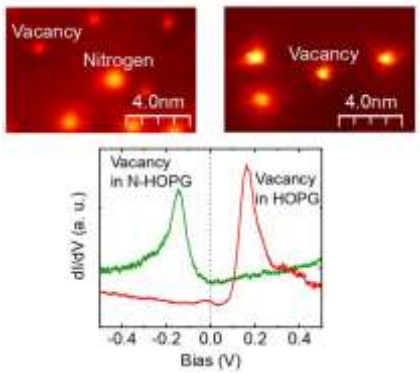

Figure 1: STM images of Vacancy on HOPG with and without Nitrogen doping (V = 0.5 V, I = 100 pA). dI /dV spectra of vacancy sites measured on both cases.