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MS-2-O-3480 Plasmon Tailoring in Graphene through Lattice Impurities and Ad-Atoms

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Although there is considerable documentation on efforts to tailor and employ plasmons to merge photonics and electronics, and use surface plasmons for subwavelength optics [1,2] and enhancement of the photovoltaic conversion efficiency, especially by making use of the surface plasmons at metal nano-clusters [3], little has been reported on single atom plasmon effects [4]. Graphene's potential for terahertz nano-scale plasmonic devices, has so far only been realised via gating and patterning [5,6]. However, defects in the graphitic plane, including vacancies and dopant atoms, can intrinsically alter the electronic structure and hence lead to effects such as plasmon enhancement and change of the plasmon energy in the uv/vis region, a phenomenon that can be exploited for coupling with light.

We present observations, using high resolution (S)TEM in combination with electron energy loss spectroscopy and energy filtered imaging, of the effects of single or few-atom impurities on plasmons in the uv/pi-plasmon energy regime in graphene. We accompany the experiments by WIEN calculations, which reveal new transitions in graphene for various metal ad-atoms species (Ti, Pd) and also for Si (fig. 1) and substitutional dopants such as B and N: a peak at around 1-2 eV is introduced which is not present in energy loss spectra of pristine graphene. Both, position and intensity of this peak change according to doping/dosing levels. The increase of the latter shifts this peak towards the uv regime (3eV). These transitions are mostly ascribed to single particle (SPE) and intraband excitations or to SPE-π plasmon coupling and not to the creation of new plasmon peaks in the graphene-dopant system. The same applies to defect and edge-states. Our experimental observations are in general support of the above predicted additional absorption features in the uv. More so, we observe intensity enhancement around metal atoms (e.g., Pd) at graphene edges (fig. 2), which we also find, although to a much lesser extent, at pristine graphene edges. This intensity increase does, however, not arise from new spectral features and is ascribed to the enhancement of intrinsic low loss features of graphene, where metal atoms/ defects act as atomic antennae, due to donation of d-electrons, in the case of transition metals. The efficiency of this process appears to vary with the transition metal, and seems to be high for, e.g., Pd.

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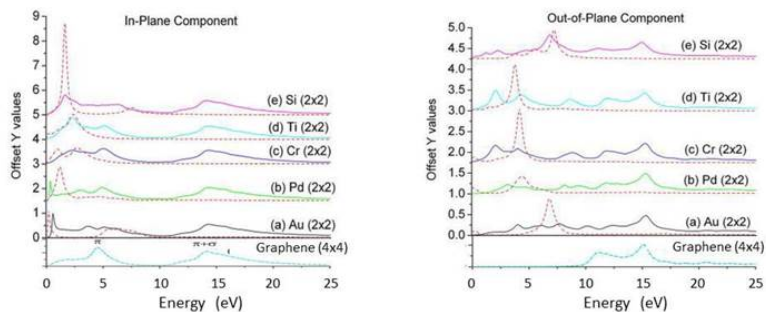[6] L Ju et al Nature Nanotech, DOI: 10.1038/NNANO (2011) 146

Fig. 1: Simulated in-plane (left) and out-of-plane (right) EEL spectra of a single (a) Au, (b) Pd, (c) Cr, (d) Ti and (e) Si adatom on (solid curves) and spectra after the carbon atoms of the graphene are removed (red dashed curves). Spectra are shifted along the Y axis and are all on the same scale. The two bottom spectra are of pristine graphene.
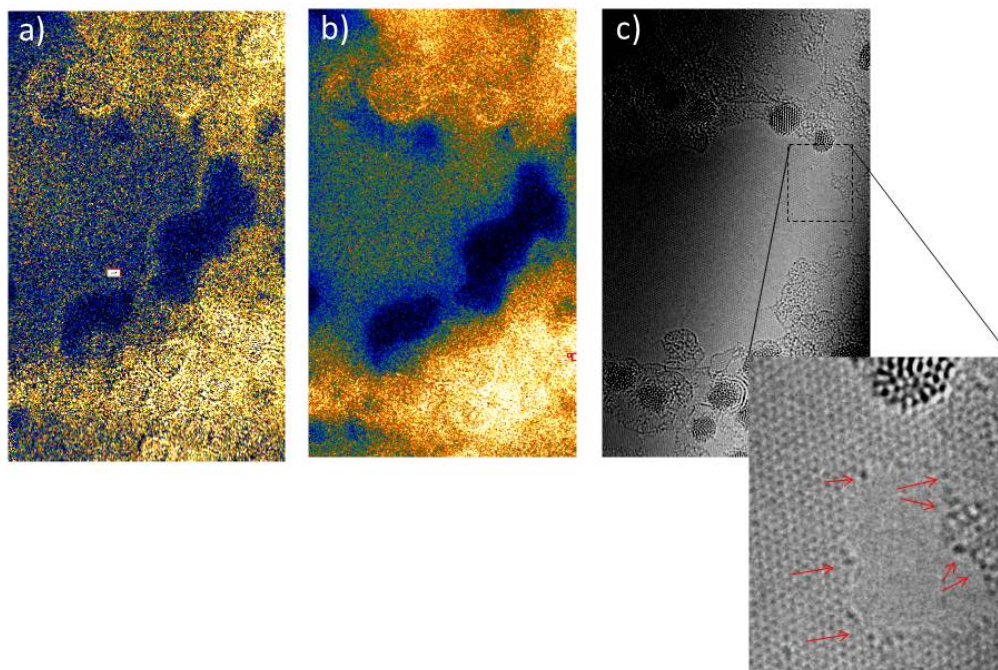

Fig. 2: Images from an EFTEM image series obtained in a monochromated triple -corrected Titan-PICO: a) enhancement at 3.5-4 eV and b) depletion at 5-5.5 eV of the loss intensity at a hole in graphene with Pd deposit, c) HREM image prior to the EFTEM series with magnified boxed area, showing Pd atoms (arrowed) decorating the edge of the hole.