Atomic scale imaging and spectroscopy of 2D silica glass on graphene

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Low dimensional materials such as carbon nanotubes, graphene and hexagonal boron nitride open new frontiers to TEM research as, for the first time it is now possible to study the crystal surface in transmission mode and see individual atoms instead of atomic columns. This has resulted in a huge variety of recent scientific studies that would have been impossible to think about before, such as identification of single point defects e.g. [1], the precise determination of nitrogen and boron sites in h-BN by ADF [2], the detection of charge redistribution due to chemical bonding in direct HRTEM images [3] and single atom EELS [4]. All of these have in common that without the invention of aberration-correction they would be impossible as it is necessary to work at low electron energies to avoid destruction of the specimen by knock-on damage [5].

To date, most of the 2D materials studied by TEM were crystalline and, despite the huge improvements in machinery during the last decades, direct imaging of individual atoms in unordered 3D materials has not been possible so far as only the 2D projections are observed. This projection problem can be sidestepped by working on 2D unordered systems such as amorphized graphene [6] or 2D oxide glasses that have recently been synthesized on metal surfaces [7]. We found that a 2D silica layer was formed on graphene during a CVD growth on Cu foil. Here we show that this allows atom-by-atom (S)TEM imaging and spectroscopy of the glass [8].

The structural images obtained by TEM shown in figure 1 strikingly resembles Zachariasen's cartoons of the atomic arrangements in glass from 1932 [9]. From these images, simply by measuring the atomic positions, it is possible to directly extract ring statistics and higher order correlation functions previously restricted to computer simulations. The composition and bonding of the glass was determined by aberration-corrected EELS mapping (see figure 2). From the near edge core loss structure we find that it is built from (SiO₄)²⁻ tetrahedra and is not covalently bonded to the carbon support. The out-of-plane structure was determined by combining several techniques such as analysis of ADF intensity, oxygen K-edge structure and side-view imaging of the material. All experiments indicate that the structure consists of a bi-tetrahedral layer of SiO₂.

These results demonstrate that atomic resolution imaging and spectroscopy of a 2D glass on graphene is possible. Interestingly, the graphene, besides providing a mechanical support, freeing the silica from the requirement of extreme mechanical stability, plays an important role by energetically stabilizing the 2D silica with respect to bulk SiO₂ via van der Waals interactions, as indicated by DFT simulations.

References

[5] JC Meyer et al., PRL accepted (arxiv 1203.2372)
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**Figure 1.** a,b) Zachariasen’s model of atomic arrangements in glass. c,d) Experimental HRTEM images of silica glass on graphene – scale bars 5Å. e,f) Nano-beam diffraction pattern of crystalline and amorphous areas.

**Figure 2.** a) ADF STEM overview image of 2D silica on graphene. b) Structure model of bi-tetrahedral layer of silica. c) simultaneous ADF image and d) Si, O, and C composition maps extracted from EELS spectrum imaging – scale bar 2 nm. e) Silicon signal separated into SiO$_2$-like (green) and SiC-like (white) using multivariate curve resolution.