Atomic imaging and spectroscopy of defects in low-dimensional materials

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Abstract

Atomic defects or edge structures are important in crystalline materials, and especially in low-dimensional ones, since the interrupted periodicities strongly affect their physical and/or chemical properties. In bulk crystals, electron microscopes have been widely used to examine structural defects such as dislocations and grain boundaries, which are regarded as one- and two-dimensional structural defects, respectively. In contrast, individual point defects (zero-dimensional defects such as mono-vacancies, impurity/dopant atoms) were believed to be difficult to investigate, with both atomic sensitivity and atomic resolution required in the analytical techniques employed. In addition, the specimens need to be very thin in order to detect the individual point defects from image contrast in transmission electron microscopy (TEM).

After a monovacancy was first observed by TEM and proved to be stable even in low-dimensional carbon structures [1], studies of point defects in mono-layered materials have become very popular among scientists. Vacancies and topological defects in graphene are commonly examined at atomic level [2, 3, 4]. Defects and edge structures in hexagonal boron nitride (h-BN) are also a hot topic among physicists [5, 6, 7, 8]. Recently, mono-vacancies have been successfully identified in WS_2 nano-ribbons [9].

Here we describe HR-TEM and spatially resolved EELS studies of various single-layered materials with the interrupted periodicities. Atomic defects and edge structures can be unambiguously identified with the elemental assignment. The inevitable delocalization of EELS signals is suggested to practically limit the achievement of using EELS for chemical mapping with atomic resolution. The boron monovacancy (V_B) is assigned as a typical point defect by ADF imaging and EELS, and energy-loss near edge fine structure (ELNES) is used to investigate the electronic states of nitrogen atoms around the point defect. The work provides an example of spectroscopic imaging based on the scanning transmission electron microscopy (STEM)-EELS techniques to demonstrate the possibilities of exploring the electronic states with single atom sensitivity.

A JEM-2100F equipped with a delta corrector and cold field emission gun was operated at 60kV for these spectroscopy experiments [10]. A fast Frourier transform (FFT) of the typical ADF image shows that the microscope can resolve 0.108 nm in the STEM mode. The probe current was ~ 40 pA. In this condition the single atom spectroscopy at the graphene edge becomes feasible and shows distinct properties of edge carbon atoms [11].

Here we will show our recent progress in electron microscopy and its *in situ* investigations to visualize the various atomic defects in the low-dimensional carbon or non-carbon nanostructures. The monovacancy analysis in h-BN single-layer [12] and the alloying and doping behaviors of $Mo_xW_{1-x}S_2$ single-layers [13] will be presented.

References

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Figures

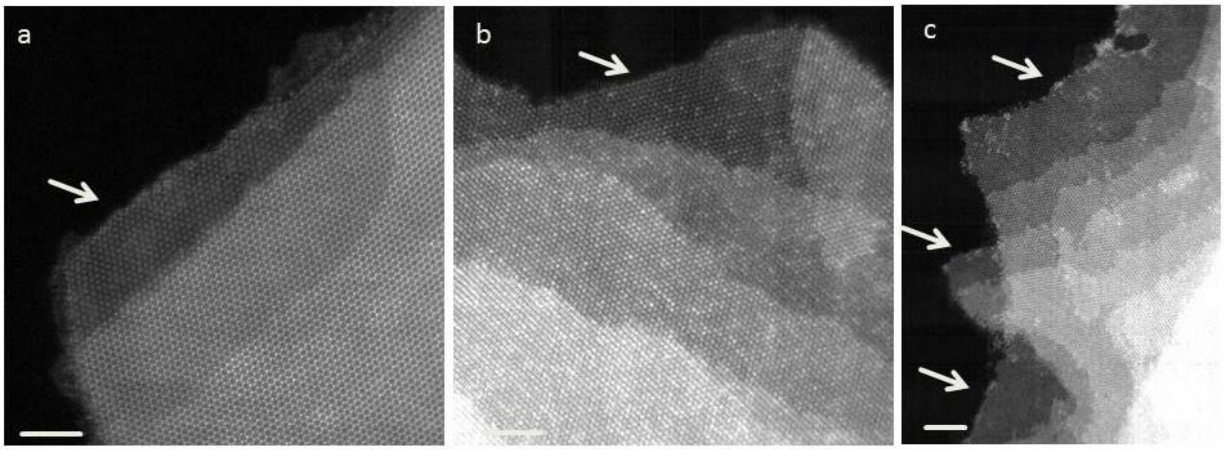

Fig. 1. Cleaved Mo1-*x*W*x*S2 specimens with single- to few-layered regions [13]. (a, b, c) Examples of scanning transmission electron microscope annular dark-field images of mixed Mo1-*x*W*x*S2 layers (*x* = 0, 0.2, and 1). *x* refers to the starting materials. The single-layer regions are marked with white arrows. Scale bars = 3 nm. Note that some regions with less contrast and no periodic structure are the amorphous carbon layers of inevitable contamination during the transfer process.

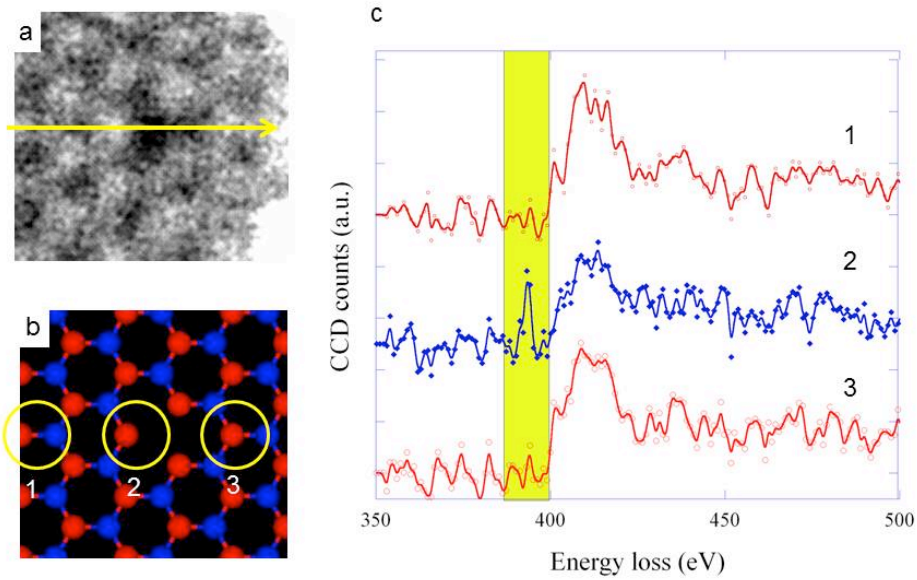

Fig. 2 Monovacancy in h-BN layer [12]. (a) ADF image shows a monovacacny in a single layer h-BN. Line-spectrum was recorded along the yellow line. (b) Schematic presentation (red: nitrogen, blue: boron) of boron monovacancy. (c) Nitrogen *K*-edge fine structures extracted from the line-spectrum. Each of three approximately corresponds to the probe positions marked in (b). A prominent prepeak in the nitrogen *K*-edge can be found at 392 eV in the spectrum recorded at the position 2, i.e., near the boron vacancy site.