Structural properties of novel tungsten nitride nanosheets

Wenzel, O.[1]

[1] Laboratory for Electron Microscopy, Karlsruhe Institute of Technology (KIT), Germany

Tungsten nitride (WN) is a popular compound in microelectronics due to its favorable material properties such as high melting point, tremendous hardness and good electrical conductivity. Despite its widespread application, thin sheets of WN could not be synthesized up to now due to the high reactivity of the material with oxygen. This work focuses on structural, chemical and optoelectronic properties of WN nanosheets, which were synthesized with an alkylamide synthesis. The materials 2D shape was obtained by passivating its (001) lattice plane with a long-chain amide surfactant during crystallization and therefore, forcing crystal growth parallel to the basal plane of its hexagonal crystal structure. Synthesis and sample preparation were performed in an argon atmosphere (Schlenk line and glove-box) with the aid of a transfer TEM holder to protect the material from oxidation and hydrolysis. Electron microscopic techniques comprising scanning, high-resolution and scanning transmission electron microscopy (SEM, HRTEM, STEM) and electron spectroscopy (EELS, EDXS) were performed to determine structure, morphology, electronic properties, as well as chemical composition. These studies were accompanied by X-ray powder diffraction (XRD) and gas adsorption (BET) measurements.

The crystal structure was determined with Fourier transform (FT) analysis (Fig. 1b) of HRTEM images (Fig. 1a), as well as XRD. Both methods demonstrate the dominant phase to be hexagonal WN (P-6m2, 187) [ICSD: 76005]. According to Fig. 1b, the sheets grow along the (001) basal plane. Simulations with JEMS [1] assuming 3 nm thickness, -8 nm defocus and Cs 0 demonstrate that the WN nanosheets consist of a honeycomb structure of alternating W (light-grey) and N (grey) atom columns (Fig. 1d). Stacking faults (Fig. 1a) can sometimes be seen on (-110) and (100) planes. The WN nanosheets have an irregular hexagonal shape with mostly straight boundaries. The lateral extension of these sheets ranges from 10 nm up to 150 nm with 1.8-3.2 nm thickness, which was measured from upward-bent nanosheets. In SEM images, stacks of WN sheets with widths of around 3-4 m are visible, too. These nanosheets are stacked in [001] direction, however, they are occasionally rotated 4 - 20° to one another in the basal plane (Fig. 2b). This rotation gives rise to characteristic Moiré effects visible in Fig. 2a. EDXS analysis of WN aggregates shows a high degree in purity, especially with respect to O, whilst having a surface area of 115 m^2/g as determined with BET. Further, the shape of the EELS N-K edge is in good agreement with reported XPS and EELS data.

This study shows that, for the first time, WN was successfully synthesized as nanosheets. Looking ahead, this technique should also be applicable to other transition metal nitrides, which opens up the possibility of a still yet unexplored new class of 2D materials.

[1] P.A. Stadelmann, Ultramicroscopy. 21 (1987) 131 - 145.

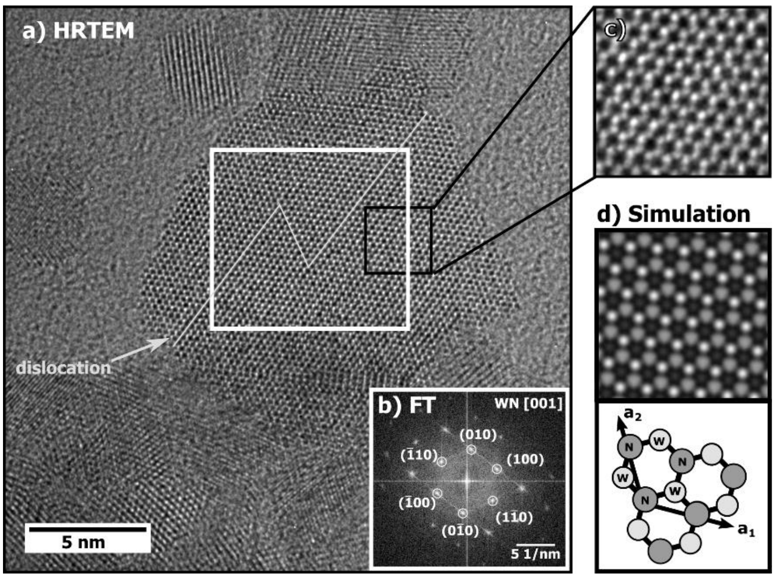

Figure 1. (a) WN nanosheet with Fourier transform (b), close-up (c) and JEMS [1] simulation (d).

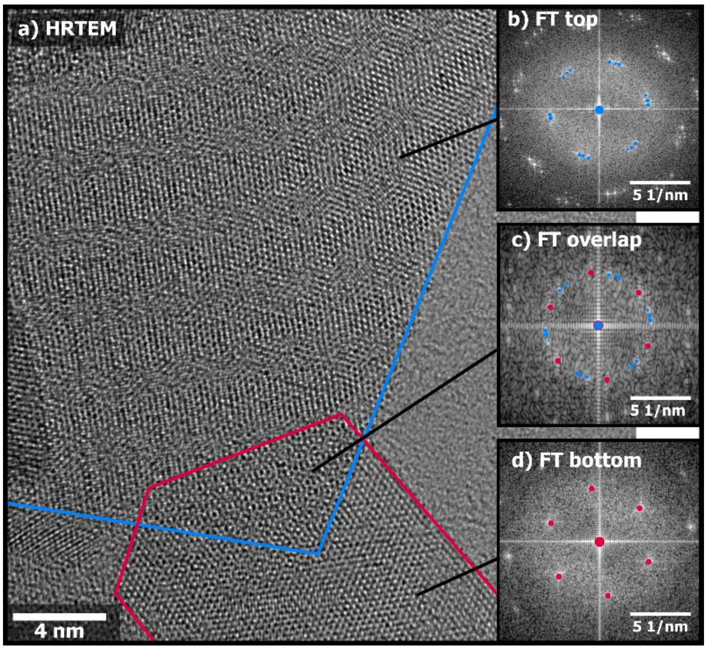

Figure 2. Characteristic Moiré pattern due to overlap of WN nanosheets (a) with Fourier transforms of different regions (b-d).