A. Composition and crystalline structure of nanowires containing radial and axial (Cd,Zn)Te insertions grown at 290 °C

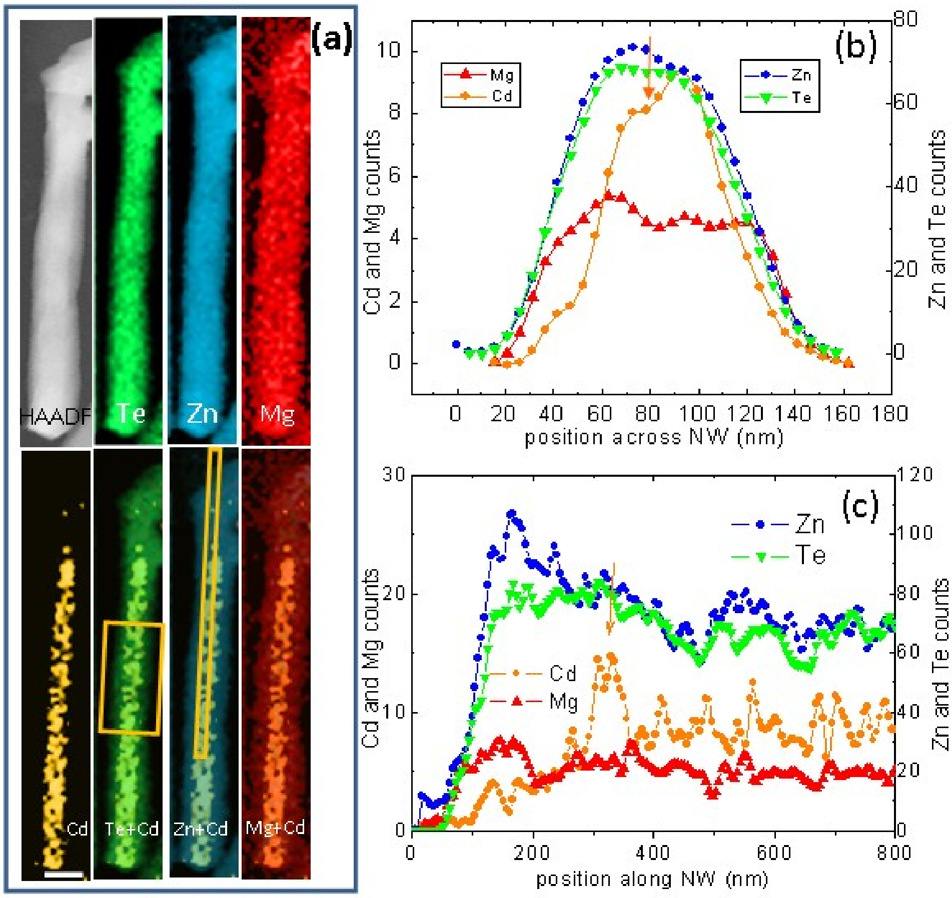

Figure I. Energy dispersive X-ray spectroscopy (EDS) images for a nanowire containing a radial (Cd,Zn)Te-shell grown at 290 °C (a) EDS integrated intensity maps for Te-L, Zn-K, Mg-K and Cd-L spectral lines, the comparison of Cd and (Te, Zn, Mg) distributions and the high-angle annular dark-field (HAADF) image performed on the scanning transmission electron microscope (STEM) (b) EDS profiles (averaged along the nanowire axis in a yellow frame shown in Te+Cd map), (c) EDS profiles (averaged across the NW in the yellow frame shown in Zn+Cd map). The scale bar is 100 nm.

In Figure I, the energy dispersive X-ray spectroscopy (EDS) measurements for a nanowire in which the CdTe insertion is deposited at 290 °C are summarized. The distribution of Cd, Zn, Te, Mg EDS-elemental spectral lines are shown together with the high angle annular dark-field (HAADF) image of the investigated nanowire. The data shows clearly the location of the Cd shell around the ZnTe core. This shell starts at the bottom of the nanowire and ends about 300 nm below the top of the nanowire.

A more detailed analysis of the EDS profiles performed in the direction perpendicular to the nanowire axis is shown in Figure Ib. The full width at half maximum (FWHM) of the Cd-signal intensity is 55 nm. The shape of the Cd-signal curve in which a minimum intensity at the nanowire center (marked with an arrow) can be deduced suggests the presence the of core/shell geometry. Moreover, the asymmetry of the thickness or the composition of the Cd-rich shell can be deduced, as well. The FWHMs of Zn and Te signals are significantly larger, about 80 nm, while that of Mg signal is the largest, around 95 nm. This reflects the fact that the Cd-rich shell is further embedded in ZnTe and (Zn,Mg)Te coatings. Worth noticing is the asymmetric shape of Mg-signal and a clear minimum in the middle, which is, again, typical for the core/shell geometry.

The distribution of Cd-signal along NW (Figure Ic) indicates the presence of a maximum at 340 nm from the top of NW (marked with an arrow). This suggests a possible presence of an axially grown (Zn,Cd)Te segment on the top of the ZnTe core, from which the optical emission is observed in CL-measurements. The length of this segment is estimated to be about 80-100 nm. This information finds confirmation in EDS data from other nanowires as well (not shown).

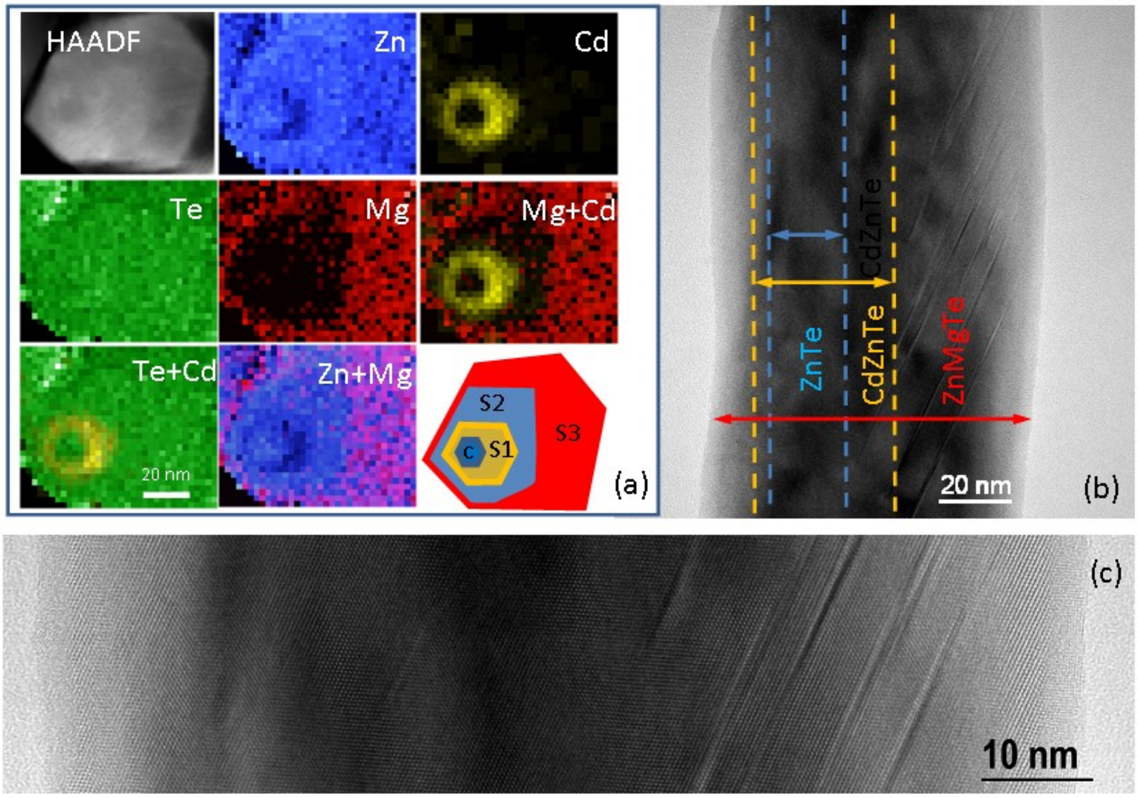

Figure II. EDS distribution maps at the NW cross-section and high resolution transmission electron microscope images (HR-TEM) for a nanowire containing radial (Cd,Zn)Te shell deposited at 290 °C (a) EDS quantitative distribution maps of elements on a cross-section of NW with a schematic representation of the observed shells; (b) <110> zone axis HR-TEM image of NW with marked hypothetical position of ZnTe core and CdZnTe shell; (c) A zoomed part of the HRTEM image showing both sides of NW.

The cross-section of the nanowire is obtained by a classical TEM preparation method usually used for the preparation of epitaxial layers involving mechanical polishing and Argon-ion milling. In Figure IIa, the

HAADF image and EDS elemental distribution maps of the individual NW cross-section are shown. During EDS-mapping, the surface normal direction is fixed to (111)-zone axis, i.e., perpendicular to the nanowire axis. In the HAADF image (Fig. IIa) one can recognize a hexagonal shape, the cross-section, however, deviates rather strongly from symmetric shape for this particular nanowire.

The elemental distribution maps allow to distinguish each shell's shape, width and elemental composition. In particular, the presence of the (Cd,Zn)Te radial shell (S1) is clearly demonstrated. The (Cd,Zn)Te shell's (S1) thickness vary from 5 to 20 nm, whereas the average concentration of Cd atoms in S1 is about 0.2, while the maximum measured value is 0.4 in the asymmetrically extended part of the shell. The difference in the composition can be related to the interdiffusion of Zn and Cd and the highly directional growth of ZnTe and (Zn,Mg)Te shells in a molecular beam epitaxy process. The next shell (S2) consists mostly of pure ZnTe and is deposited simultaneously with the upper ZnTe segment. The external (Zn,Mg)Te shell (S3) shows a strong asymmetry as well, with the thickness ranging from 5 to 30 nm. The mean concentration of Mg in the (Zn,Mg)Te-shell is about $x=0.14$.

High resolution transmission electron microscope (HR-TEM) images of a similar NW in the <110> zone axis are shown on Figure IIb and IIc. In both nanowires some stacking faults (SF) on the right-hand side of the image can be noticed, whereas on the left-hand side no defects are observed. The defects propagate mostly in the (Zn,Mg)Te coating shell, in particular, when its thickness becomes relatively large. This could be associated to a strain relaxation process which may occur while the shell exceeds a certain critical thickness. Most importantly, the (Cd,Zn)Te shell (S1) is found to be free of stacking faults in several nanowires, which makes the observation of optical emission from these structures possible.

B. Composition and crystalline structure of nanowires containing axial (Cd,Zn)Te insertions only, grown at 350 °C

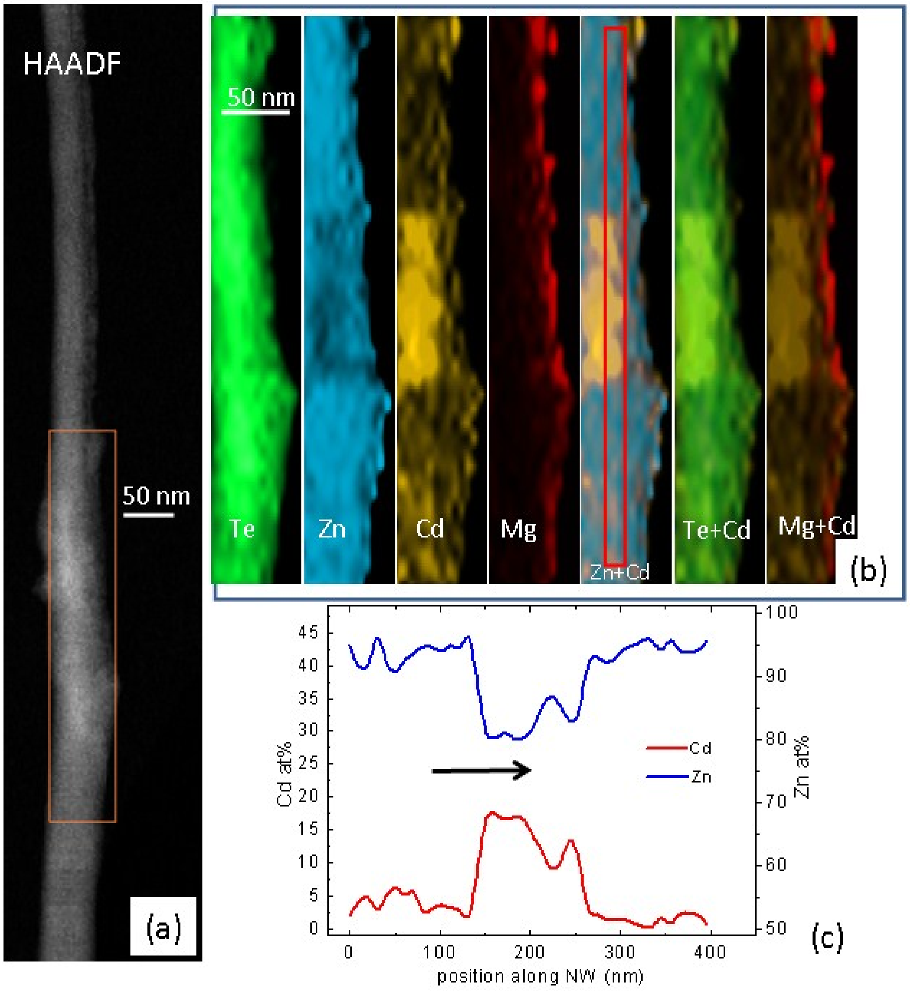

Figure III. EDS results for a nanowire containing a Cd-rich axial insertion grown at 350 °C (a) HAADF image (b) maps of integrated intensity distribution of EDS elemental spectral lines for Te-L, Zn-K, Mg-K and Cd-L. (c) Profiles of the characteristic EDS elemental spectral lines for Zn and Cd along the Cd-rich segment (averaged in the frame shown in Zn+Cd map)

Elements distribution maps presented in Figure III reveal the presence of axial (Cd,Zn)Te insertion only, in the case of nanowires in which the CdTe insertion is deposited at 350°C. There is no significant deposition of Cd atoms along the nanowire axis which would lead to the formation of a radial (Cd,Zn)Te shell. This result confirms basically the CL-data presented in the paper. The average profiles of Cd and Zn signal distribution, see Figure IIIc, show that the length of the investigated (Cd,Zn)Te insertion is about 120 nm. The average Cd content in the insertion is estimated to be in the range 0.4-0.6, after taking into account the presence of the (Zn,Mg)Te coating shell. The position of the Cd-rich insertion is found to be about 600 nm from the top of NW. The (Zn,Mg)Te shell is relatively thin in the particular case of the nanowire under investigation, about 5 nm to 10 nm.

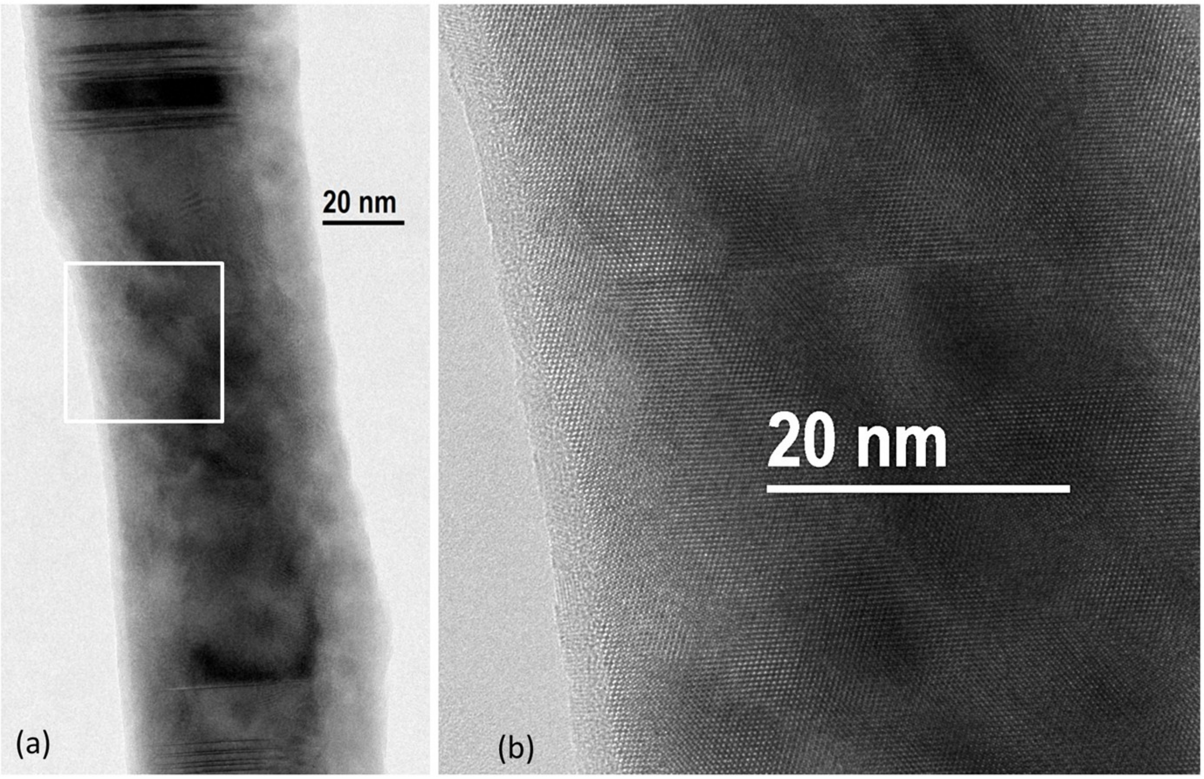

Figure IV. (a) High resolution transmission electron microscope images of a nanowire containing an axial (Cd,Zn)Te insertion (b) zoom on the frame from (a) which corresponds to the position of the Cd-rich insertion showing structural details including one stacking fault.

In case of several nanowires, HR-TEM pictures reveal an almost defect free crystalline structure at the areas corresponding to the (Cd,Zn)Te axial insertions. In other structures a few stacking faults can be found, as exemplified in Figure IVb. This could be the reason, that the CL emission from axial insertions is not observed in all nanowires under investigation. In fact, about 50% of the nanowires from this sample do not emit light at energies corresponding to the (Cd,Zn)Te insertions. The correlation of structural and optical properties is, however, out of the scope of the present paper. Interestingly, we note that the presence of Cd rich (Cd,Zn)Te axial insertions has generally a beneficial impact on the number of stacking faults. This aspect should be a subject of future investigations.