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Nanocavity Networks by Folding Sheets of Layered Crystals

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Practical applications of tubes almost always depend on the possibility that one can form junctions with other tubes and link them into meaningful networks. On the nanoscale, this is a current challenge. Here we report a new approach [1]. Rather than starting from the more common cylindrical nanotubes, which are essentially rolled-up sheets of layered crystals, we show how one can fabricate nano-sized tubes with prismatic cross-sections by inducing patterns of folds in the near-surface region of layered crystals. This is achieved by exploiting the phenomenon that certain metal atoms deposited onto layered crystals intercalate into the top-most layers and build up compressive stress. Spontaneous relaxation of this stress leads to the formation of remarkably regular fold structures composed of linear channels that are interconnected in hexagonal networks.

We deposited Cu onto freshly cleaved surfaces of layered VSe_2. During deposition the surface was monitored by in-situ LEEM. The nanofold patterns form suddenly after depositing a dose of Cu that corresponds to a nominal layer of a few nanometers (Fig. 1A). The fold pattern shows hexagonal symmetry with many regular nodes (Fig. 1B). In order to reveal the fold morphology we prepared cross-section samples for HRTEM using a shadow-FIB technique (Fig. 2A), which does not require protection of the surface with Pt. HRTEM clearly shows that the surface folds cover nano-scale cavities (Fig. 2C). From such cross section images the shape, size and structure of the nanofolds can be measured directly. It is apparent that the cavity has a triangular cross section enclosing 30° angles at the base and a 120° angle at the top. This indicates a crystallographic alignment of the layer segments that comprise the fold. The thickness of the layer is about 10nm, and the roof segments appear to have a transformed crystal structure. This aspect of the nanofolds is under continued investigation.

Plan-view TEM analyses show that the nanofolds are aligned along low-index crystal directions of the substrate (Fig. 3A). Our observations are consistent with a model in which the metal atoms intercalate into the crystal [1], forming a thin layer with laterally expanded lattice (Fig. 3B). The nanofold pattern formation results from the relaxation of compressive stress that builds up during the intercalation reaction.

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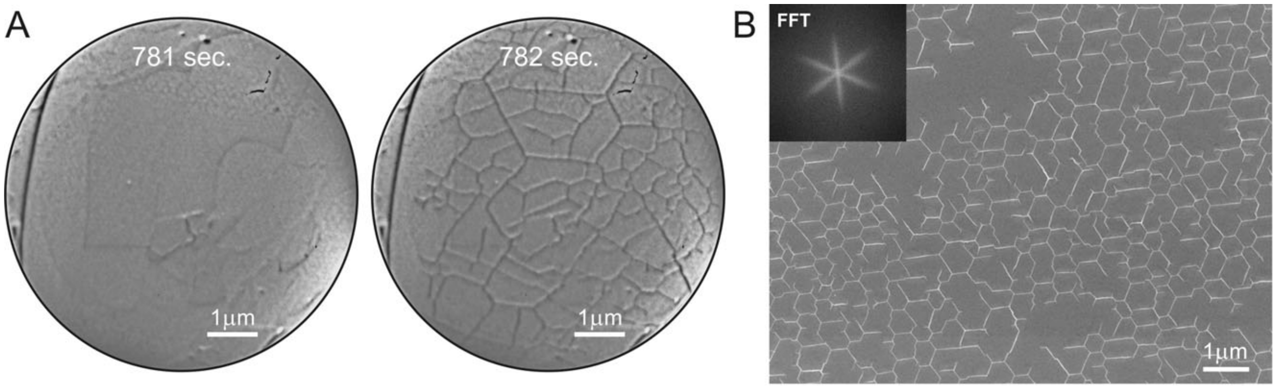

Fig.1 A: In-situ LEEM observation of the rapid formation (within 1 second, after 780 seconds incubation time) of a pattern of surface nanofolds on layered VSe_2. B: SEM-image showing a typical network area with hexagonal symmetry (inset: FFT).

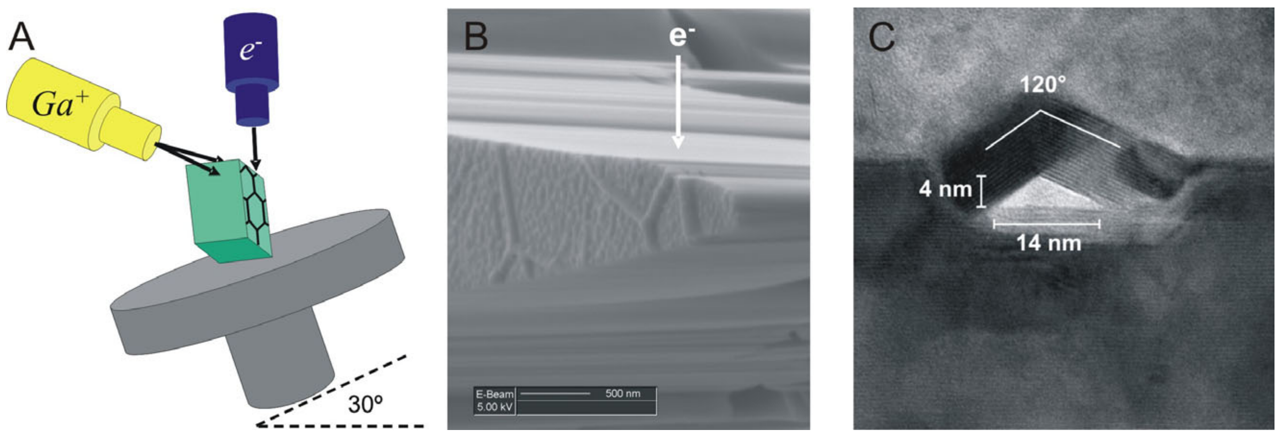

Fig.2 A: Cross-sectioning by the shadow-FIB technique (schematic), B: SEM-image of sample tip produced by the technique, C: HRTEM-image of a nanofold with prismatic cavity.

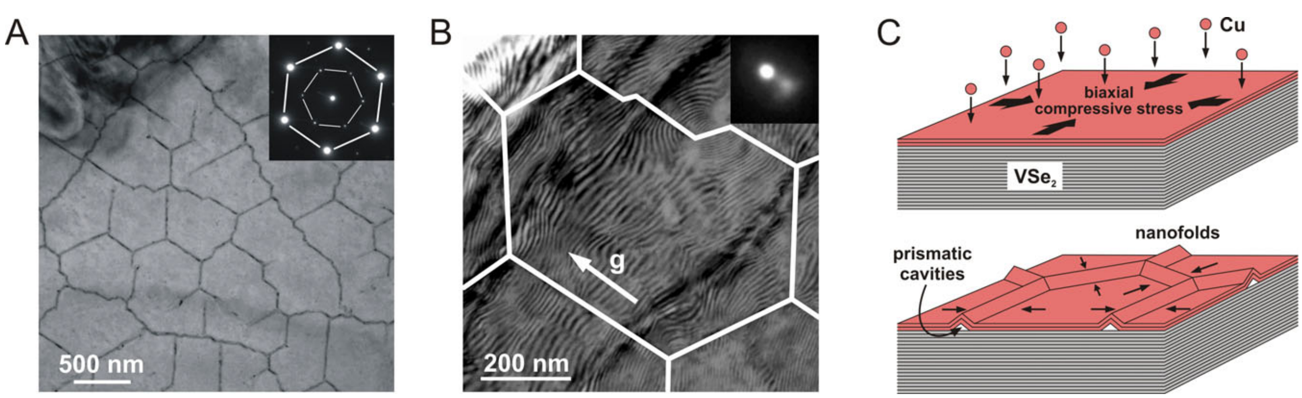

Fig.3 A: Plan-view TEM BF-image and diffraction pattern showing that the nanofolds are aligned along low-index substrate directions. B: Moiré-pattern in a BF-image showing the existence of a thin surface layer with expanded lattice. C: Model explaining the formation of nanofolds with cavities as resulting from relaxation of stress that builds up during metal intercalation into the layered crystal.

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