Boomerang-shaped VO$_X$ nanocrystallites

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Abstract. "L"-shaped VO$_X$ nanobelts were obtained by hydrothermal synthesis. These nanobelts represent the first example of nano-sized objects, containing well-defined kinks. The angle was found to be $96° \pm 3°$. Here we report on initial experiments with transmission electron microscopy (TEM) and selected area electron diffraction (SAED), which revealed twinning to be the origin of the kinked structure. The interesting boomerang-shaped nanocrystallites were compared with their more widely known counterpart, the V$_2$O$_5$ nanofibers. Furthermore, thin films with areas exceeding $10 \times 10 \ \mu m^2$ have been found to be produced by the hydrothermal synthesis route. The SAED data revealed, that all three morphologies are based on a similar crystal structure.

INTRODUCTION

V$_2$O$_5$ nanofibers (see Figures 1 (a), 2 (a)) have attracted attention due to their possible use as electrostatic coatings and as building blocks in nanoelectronics [1, 2]. These nanofibers, with a width of 10 nm and a height of 2.5 nm (see inset of Figure 1 (a)), can be easily grown in aqueous solution. Their room-temperature synthesis, however, bears the drawback of a long synthesis time ($\approx$ 3 month), until they reach a length exceeding several μm.

In order to speed up the growth, a hydrothermal synthesis route was attempted to reduce the preparation time. These procedure yielded two new morphologies instead of regular nanofibers. The first morphology consists of broad bands (Figures 1 (b), 2 (b)) with a width of 500 nm, while their height matches that of the nanofibers, as displayed in the inset of Figure 1 (b). Most remarkably they appear in the shape of a boomerang, containing a kink with a reproducible angle of $96° \pm 3°$ (see Figure 1 (b)). The second new morphology, as displayed in Figure 2 (c), consists of thin films with dimensions exceeding $10 \times 10 \ \mu m^2$.

EXPERIMENTAL

For the synthesis of V$_2$O$_5$ nanofibers 0.2 g ammonium(meta)vanadate (NH$_4$VO$_3$) and 2 g acid ion exchange resin (DOWEX 50WX8-100) were added to 40 ml of water. Due to a polycondensation process, fibers are formed within an orange colored gel. In order to obtain fibers with length exceeding 5 μm, the solution is kept at ambient conditions for more than 10 weeks.

In the hydrothermal approach – used for the synthesis of the boomerang-shaped material, as well as the thin film – 150 μl of vanadium-oxytriisopropoxide have been mixed with 15 ml of water. The mixture was stirred at 70-80 °C until the vanadium-precursor
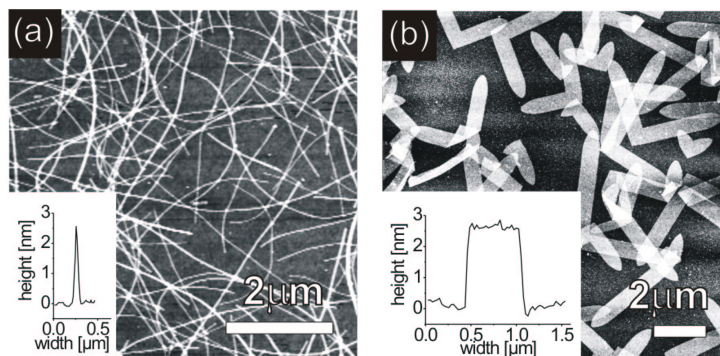
FIGURE 1. Atomic force microscopy images of V_2O_5 nanofibers (a) and boomerang-shaped VO_X nanocrystallites (b). The inset of the images display the cross-sections of the corresponding material

completely dissolved in the solvent. The solution was transferred in an autoclave cell and heated for 3.5 h at 180 °C.

The obtained vanadiumoxide dispersions were dip-coated on amino-silanized SiO_2-wafers and Formvar-coated copper-grids for AFM- and TEM-experiments, respectively. AFM-measurements have been performed on a DI Nanoscope IIIa, while TEM and SAED have been carried out on a Philips CM30/ST (300 kV). See Reference [3] for details.

RESULTS AND DISCUSSION

Figure 2 compares the morphology (a-c) and SAED pattern (d-f) of the three species. The [001]-diffraction pattern of an isolated L-shaped species (Figure 2 (e)) attests the monocrystallinity within an arm of the nanobelts. This pattern is in accordance to a pattern simulation based on the model of $V_2O_5 \cdot n \; H_2O$ xerogel [4], (assuming lattice-parameters a=12.55 Å, c=3.76 Å, $C2/m$). As the nanofibers of Figure 2 (a) are randomly oriented within the selected area used for the diffraction, a powder-like diffraction pattern is observed (Figure 2 (d)). The diffraction fringes of the fibers are in accordance to the diffraction spots of the boomerang-shaped nanocrystallites as indicated with the dashed-lines in both diffraction patterns. In addition, the diffraction pattern of the thin film (Figure 2 (f)) is in close agreement to that of the monocrystalline L-shaped material. However, one observes a double spot feature, where the two spots are related to each other by a small angle of rotation ($\sim 5°$). This phenomenon can be attributed from the wrinkled structure of the foil and the resulting superposition of two layers whose planes are rotated relative to each other by the specified angle. Despite their different morphology, all three species have the same crystal structure along the [001] direction, which is in accordance to that reported previously by Petkov et al. [4]. It should be stressed, that supplementary experiments are needed in order to access the third dimension.

In order to elucidate the origin of the kinked morphology, we recorded a detailed series of SAED-patterns along an isolated boomerang-shaped nanobelt [3]. From this
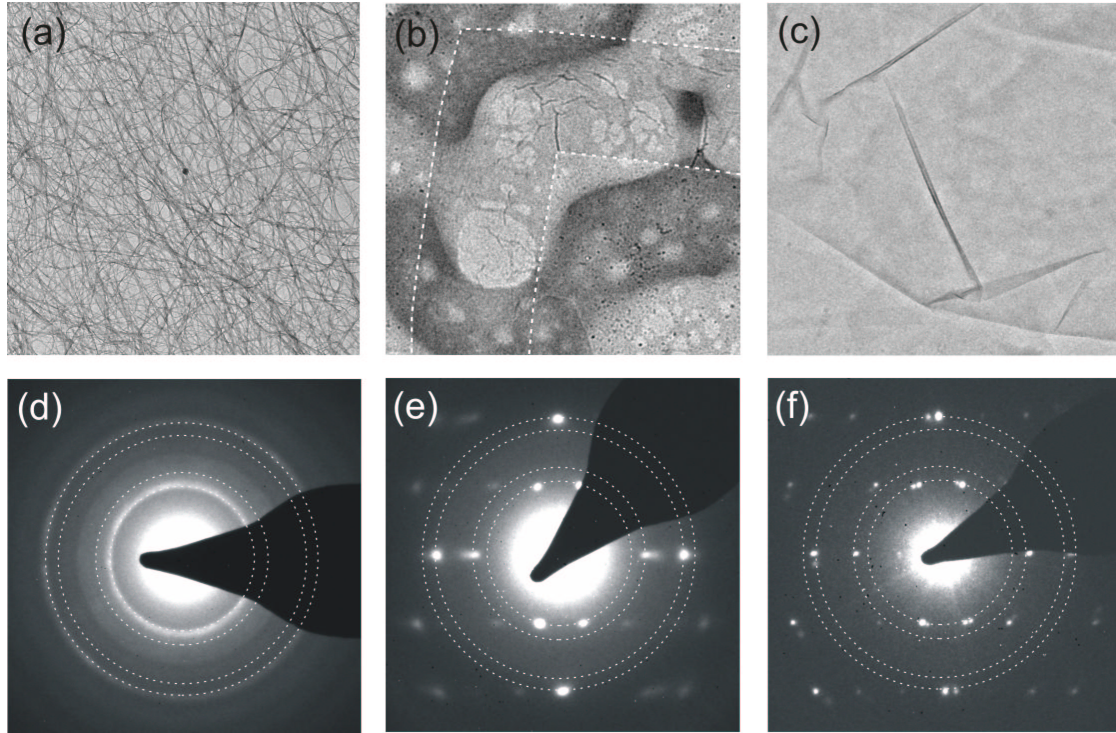
FIGURE 2. Transmission Electron Microscopy (TEM) Images of V_2O_5 nanofibers (a), boomerang-shaped VO_X nanocrystallites (b), and VO_X foil (c). The image size is 2.4 μm each. Selected Area Electron Diffraction (SAED) of an agglomerate of nanofibers (d), an isolated arm of a boomerang-shaped nanocrystallite (e), and a folded region within the foil (f)

analysis it became evident, that the SAED-pattern obtained in the center of the nanobelt is a superposition of the distinct patterns of the two arms [3]. It is therefore concluded, that twinning is the origin of the kinked structure. Similar twins have previously been found in V_2O_5-crystals [5].

The twinning-direction can be determined from the superimposed pattern of the center region (Figure 3 (a)). For comparison, Figure 3 (b) shows the simulated pattern of the central region, which is based on the model of Petkov et al. [4]. Whereas the spots of only one color (black or gray) are giving rise to the diffraction pattern of an isolated arm (as diplayed in Figure 2 (e)), the sum of both patterns is required to reproduce the superimposed pattern observed in the center of the kink (Figure 3 (a)).

The spots along the vertical axis belong to both patterns as indicated with the two-colored circles. Therefore this direction is the twinning-axis. Based on the $[010]^*_{1,2}$ directions in reciprocal space, the twinning axis can be identified to be $[310]^*$ in reciprocal space, corresponding to $[130]$ in direct space. The angle between the $[010]^*_{1,2}$ directions in reciprocal space is found to be $84°$ and agrees well with the angle of $96°$ observed in direct space (Figures 1 (b), 2 (b)).
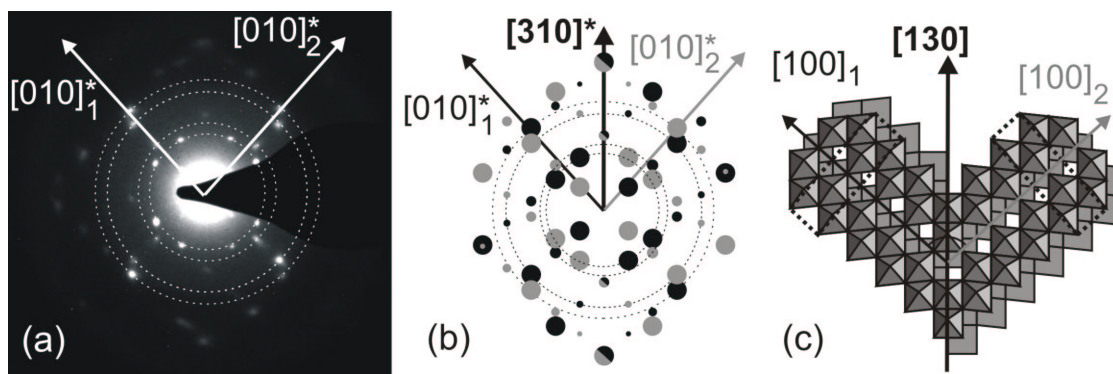
FIGURE 3. (a) SAED-pattern of the center position of a boomerang-shaped VO_X nanocrystallite. (b) Simulated SAED pattern of two V_2O_5 crystals, twinned along the [310]* orientation (vertical direction). (c) Model of the twin boundary region, the dashed box corresponds to the unit cell of each arm

CONCLUSION

Despite their different morphologies, V_2O_5 nanofibers, boomerang-shaped VO_X nano-crystallites and VO_X foils have a similar crystal structure. The kinked structure of the L-shaped nanobelts could be identified to originate from a twinning along the [130] direction. Based on the crystal-model of Petkov et al. [4], we propose a structural model of the kinked region [3]. The model as depicted in Figure 3 (c) is built up of two layers. Each layer consists of edge-sharing VO_5 pyramids. Slight distortions are needed in order to join together the two arms of the L-shaped nanobelt. The presence of distortions has also been observed in V_2O_5-crystals [5].

REFERENCES

1. Muster, J., Kim, G., Krstic, V., Park, J., Park, Y., Roth, S., and Burghard, M., *Adv. Mater.*, **12**, 420 (2000).
2. Kim, G., Muster, J., Krstic, V., Park, J., Park, Y., Roth, S., and Burghard, M., *Appl. Phys. Lett.*, **76**, 1875 (2000).
3. Schlecht, U., Knez, M., Duppel, V., , Kienle, L., and Burghard, M., *Appl. Phys. A*, **78**, 527 (2004).
4. Petkov, V., Trikalitis, P., Bozin, E., Billinge, S., Vogt, T., and Kanatzidis, M., *J. Am. Chem. Soc.*, **124**, 10157 (2002).
5. Hyde, B., and Tilley, R., *Phys. Stat. Sol. (a)*, **2**, 749 (1970).