A.10: Topotaxial growth of α -Fe_2O_3 nanowires on iron substrate

Metal oxide nanowires have attracted tremendous interest owing to their large surface to volume ratio and semiconducting properties with an optical gap typically in the visible region. Thermal annealing is among the simplest methods of synthesizing these nanowires. It involves annealing of a pure metal foil at an optimized annealing temperature and ambient, thereby producing dense metal oxide nanowires of high crystalline quality. The growth mechanism of the nanowires in this method is still not fully understood. α -Fe_2O_3 nanowires system is a typical example. It is a technologically important material and its nanowires have been used in sensors, field emission devices, photo-detectors etc. The motivation of the present work is to understand the growth mechanism in α -Fe_2O_3 nanowire system. α -Fe_2O_3 nanowires are grown by annealing iron foil at 700 °C in a flow of moist oxygen. These nanowires invariably grow along the [110] direction. In our earlier work, it was found that [110] orientation of grains of iron foil is necessary for the growth of these nanowires. To understand this type of growth behavior and the general mechanism of growth, cross-sectional Transmission Electron Microscope (XTEM) study was carried out on as-grown nanowires samples.

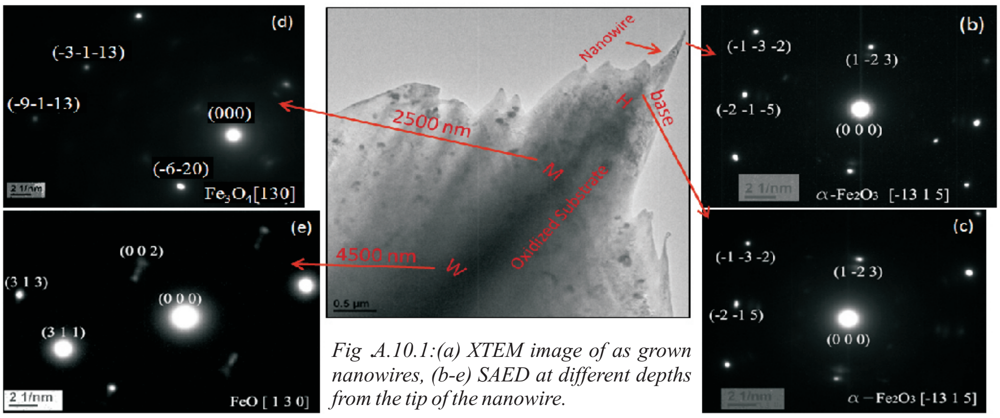

Fig. A.10.1:(a) XTEM image of as grown nanowires, (b-e) SAED at different depths from the tip of the nanowire.

X-ray diffraction measurements of these nanowires show that iron undergoes sequential oxidation: Fe Å FeO Å Fe_3O_4 → α -Fe_2O_3, to finally grow into the nanowires. The XTEM results (Fig. A. 10.1 (a)) show the TEM bright field image of a small α -Fe_2O_3 nanowire along with the substrate. A series of selected area electron diffraction patterns (SAED) with depth were taken to see the different oxide phases and their mutual orientation. (Figs A.10.1 (b to e)) Depth up to FeO layer could be observed and the following orientation relation between the layers was found: α -Fe_2O_3 [-13 1 5] || Fe_3O_4[130] || FeO[130]. The structures of iron oxides have two sub-lattices of oxygen anions and iron cations. Oxygen ions (size 132 pm) are very large as compared to the cations (Fe : 64 pm and Fe^{2+} : 74 pm) and are less mobile during the transformation from one oxide phase to another during oxidation or reduction. This results in the preservation of the close-packed layers of oxygen anions and their stacking direction, which governs the preferred mutual orientation between the two phases. This phenomenon is called topotaxy, and in iron oxide systems, it gives the following orientation relation: α -Fe_2O_3 [001] || Fe_3O_4 [111] || FeO [111] || Fe [110]. The orientations obtained by XTEM were compared with the topotaxial relationship and were found to be consistent. It is further shown that the Fe grain orientation of [1-10] and the Fe_2O_3 orientation of [110] satisfy the above topotaxial relationship. These results thus also explain the preferential growth on [110] oriented grains of iron. The dark field XTEM images further showed that the nanowires are in fact bicrystals and grow at the junction of a crystal twin in a twin band. The twin interfaces, which are the preferential growth sites, accelerate the crystal growth at the junction and this result in the anisotropic growth of nanowires. Present results have a very important consequence that the growth of the α -Fe_2O_3 nanowires can be controlled by controlling the texture of iron foil, thereby providing a new tool for patterning.

We also believe that twin mediated growth mechanism is an important aspect of this method, which can be extended to other systems and may provide a better control on the synthesis of nanowires by the thermal annealing method. [For more details, please refer to H. Srivastava et al., J. Appl. Phys. 119, 244311 (2016)]

Reported by:
H. Srivastava (himsri@rrcat.gov.in), A. K. Srivastava and Tapas Ganuli