In-situ Observation of the Growth of Tungsten Oxide Nanostructures.

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Summary: This paper describes a method for producing tungsten oxide nanostructures in an environmental scanning electron microscope. The growth is observed in real time and offers direct observation of the morphology of the tungsten oxide condensed onto the cooler part of a typical W Scanning Electron Microscope filament. We also find that the growth of nanostructures occurs on timescales much shorter than reported thus far. Corresponding to increasing temperatures along the tungsten filament, we find that the tungsten oxide deposits successively as nano-clusters, nano-multirods, 'pine-tree'-like structures, and ultimately as single nanowires.

1 Introduction

The research into tungsten oxide and its allotropes has been recently boosted by advances into the growth of one-dimensional tungsten oxide nanostructures and demonstration of their field-emission[1], gas-sensing[2] and electrochromic properties[3]. The route to their implementation into devices though requires large-scale synthesis. In the last five years however, there has been a significant number of papers claiming facile synthesis of tungsten oxide nanowires either using a chemical vapor deposition route, or a vapor-liquid-solid method of extracting solid nanowires out of a W-rich solution. Chemical vapour deposition appears to offer more control over the growth process[4], both through the morphology and chemical composition of the end product, as well as to offer a route to introducing dopants, such as P and K, of interest to the superconductivity community[5]. Here we show that the entire range of tungsten oxide nanostructures obtained so far can be produced within the same experimental set-up simply by varying the substrate temperature.

Figure 1: Optical micrograph of a tungsten filament following in-situ growth of tungsten oxide.

2 Experimental and Results In our experimental set-up, a tungsten SEM filament is electrically heated in a FEI Quanta 200 field-emission ESEM, operated at 0.40 mbar pressure (water vapour). Ever since the advent of tungsten-based light bulbs, it has been known that, in the presence of air, heated tungsten filaments etch and fail rapidly, hence the requirement for low-pressure inert atmospheres in light bulbs. Figure 1 shows an optical image of the filament taken after the experiment, at 15x magnification, identifying three key areas: 1) the yellow-orange product on the support pillar and the wire hanging just outside the support pillar (left); 2) the blue-black deposit starting in the vicinity of the support pillar and extending for

approximately 7mm and 3) the silver/shiny central portion, where the wire was at its hottest during the experiment. Figure 2 shows a sequence of SEM images taken at steps along the wire, starting just inside region 1 and ending just inside region 3. The origin of the position scale is taken to be the boundary between regions 1 and 2, just past the weld securing the wire to the post. The orange product (Fig. 2.1) appears with an amorphous shape, typical of WO_2 . As we start looking to the right of the post into region 2, where the colour changes to blue-black, we first encounter the same clustering as for WO_2 , but we also notice each cluster to be composed of crystal platelets, typical of W_2O_5 (Fig.2.2) Moving along the wire (and corresponding to an increased substrate temperature), the next two panels show the transformation of the spherical cluster into multiple nanorods aggregated around a central core, typical of $\text{W}_{18}\text{O}_{49}$. At 4500 μm , we can see that multiple nanorods surrounding the core no longer appear, and that the central core appears to be composed of concentric shells of increasing diameters (Fig. 2.5). Most importantly, as the temperature increases further (4500 and 5000 μm), the further nanorods no longer aggregate concentrically around the core, but grow out of it, giving it the ‘pine-tree’ appearance, in a structure similar to the fractal crystallization of ice into snowflakes, but in three dimensions. A further increase in temperature results in short and thin nanowires, growing in particular orientations that reveal the epitaxial relationship with the substrate (Fig. 2.7). At 8000 μm , only small islands are deposited, revealing the initial stages of nucleation and growth of the nanowires (Fig. 2.8). Lastly, at 8500 μm , the temperature is such that only etching occurs, as revealed by the typical faceting of the W wire (Fig. 2.9). This also allows us to view the effect of temperature

Figure 2: SEM micrographs of the observed tungsten deposits along the length of the wire (scale bar is 200nm).

Figure 3: Illustration showing the growth of the tungsten oxide nanostructures.

3 Discussion and Conclusions

As already suggested, we can reveal the assembly process of the tungsten oxide nanostructures by interpreting the thermal series in Figure 2 through the consideration of the competition between etching and deposition/condensation with wire temperature. By looking at the series in reverse order, we conclude the following, which is depicted in figure 3:

- The nucleation of the wires occurs at specific sites on the tungsten substrate (step-edges, defects, etc.) with the deposition of small islands of tungsten oxide ($\sim 20\text{-}30\text{nm}$ in diameter).
- Depending on temperature, further arrival of tungsten oxide leads to growth of nanowires or develops into quasi-aligned clusters of W_2O_5 crystallites or the random WO_2 .
- Nanowires grow out of small tungsten oxide islands in a very short time, of the order of a minute.

along the wire as the parameter primarily controlling the balance between etching and deposition/condensation, with lower temperatures favoring faster condensation rates. We therefore interpret the variance in nanostructure morphology and composition as temperature-induced phase transformations, translating into a rate of condensation of the tungsten oxide gas.

The series presented in Figure 2 is equivalent to a temperature-variable series of growth, but an exact temperature scale is not easily attributable. However, there are a number of factors that helps us appreciate the temperature qualitatively. Firstly, we know that the base temperature does not go above 400K over the short time that the filament is heated (5-10minutes). The wire is run always 0.1A just below the current at which it emits, which places the hottest part of the wire (its middle) at $\sim 1700\text{K}$. Lastly, tungsten oxide transforms to W_2O_5 at 1050K , and to $\text{W}_{19}\text{O}_{48}$ at 1300K .

- The nanowires thicken in concentric layers (see Figure 2.5, arrow) up to what appears to be a critical diameter (~250-300nm), from where they grow secondary and ternary wires at a higher temperature, whilst at the lower temperature further thickening is achieved by the outer layers ‘collapsing’ into layers upon layers of single small rods (diameters ~30-50 nm). Figure 3 shows a diagram of the proposed model, describing the thickening of the main nanowhisker up to a critical diameter, after which further material arriving deposits either as dendritic whiskers or as concentric layers of tightly-packed whiskers.

Hu et al[6] have observed hollow crystalline oxide fibers assembled from tightly-packed single whiskers, and have explained the one-dimensional growth of the fibers as a structure that maintains the dissipation of heat along the c and a axes of a single whisker. This may indicate that tungsten oxide exhibits anisotropic heat dissipation. Our results support this theory, explaining the observed concentric layer thickening, followed by further development of either tightly-packed aligned whisker layers or dendritic whisker growth.

This experiment also shows that the different nanostructures grow from the same gaseous species, as opposed to different vapors leading to different tungsten oxide deposits. Furthermore, the etching of tungsten is more likely driven by the reaction with the moisture in the air rather than the oxygen itself. Therefore, we believe the chemical route to the tungsten oxide nanostructures here is:

We have observed in-situ the growth of tungsten oxide nanostructures. The obtained product has the full range of morphologies obtained thus far, from amorphous WO_2 to cluster of crystallites of W_2O_5 , and ending with $\text{W}_{18}\text{O}_{49}$ nanowires in three types of formation: a thick central core enveloped in single whisker sheaths, dendritic “pine-trees” and single quasi-aligned whiskers. The observed growth supports the model where the one-dimensional growth is supported by the heat dissipation along the c and a axes of the single whiskers.

References

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