Characterization of Field-emission Grown Tungsten Nanowires by Transmission Electron Microscopy

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Summary

Metal nanowires grown by field-emission at different growth currents have been characterized by transmission electron microscopy. Electron diffraction reveals all nanowires to comprise predominantly polycrystalline bcc tungsten (W). Bright field images of the nanowires depict cylindrical W cores enveloped within a carbonaceous overcoat. Both W core diameter and C overcoat thickness vary with growth current in ways that are consistent with the postulated growth mechanism. Dark field imaging reveals that the mean grain size and its variation generally increase with growth current. High-resolution imaging confirms that all nanowires are polycrystalline with multiple grains spanning across the W cores.

Keywords: single nanowire, TEM, electron diffraction, EELS, imaging

Nanowires with mesoscopic diameters (1-100nm) have received growing interests due to their peculiar electronic properties that translate to immense potential for novel nanoscale device developments. Such promises, however, cannot be fully realized without the ability to synthesize single nanowires at desired locations. Recently, we have developed a method called cold field-emission induced growth that enables in situ growth of single nanowires at room temperature. Metal and composite nanowires (e.g. W, Co, Ni, Fe, C, C-W, C-Co, C-Ni etc.) are grown on a cathodic, cold-field-emission tip from gaseous organometallic or organic precursors [1]. This technique offers precise control in nanowire positioning and good nanowire-substrate contact (mechanical and electrical) [1, 2]. Metal nanowires, upon oxidation, can also function as ultrasensitive electrochemical sensors by virtue of their high surface-area-to-volume ratios. However, there is currently little knowledge on the properties of such as-grown materials. This motivated us to characterize metal nanowires grown from gaseous tungsten hexacarbonyl, W(CO)₆, ambient at different growth currents using transmission electron microscopes (TEMs).

The structure of as-grown nanowires was studied by electron diffraction. Our indexed diffraction patterns show that all specimens consist of polycrystalline bcc tungsten with reported, bulk lattice constant (3.1648 Å), Fig. 1. The polycrystallinity is due to the limited energy for atomic diffusion for room-temperature growth. The possibility of carbon and oxygen incorporation into the nanowire interior was also studied by indexing the diffraction patterns for W,C, WC and W,O. Our results indicate negligible, if any, carbide and oxide phases present in the nanowires. Bright field (BF) imaging was also carried out to study the growth morphology of tungsten nanowires. Our BF images invariably depict a dark cylindrical core (bcc W) enveloped within a layer of overcoat of much higher electron transparency (Fig. 2a), indicating the presence of two materials with very different atomic numbers as predicted by our proposed growth mechanism [1]. The overcoat enveloping the wires was identified to be predominantly carbon by electron energy-loss spectrometry (EELS), Fig. 2(b). Both W core diameter and degree of nanowire branching are found to be proportional to growth current, Fig. 3. On the other hand, the thickness of carbonaceous overcoat was found to bear no systematic relationship with the growth current, Fig. 3. All these observations support our proposed growth mechanism [1].

With polycrystalline nature of nanowires in mind, dark field (DF) imaging was performed to determine the dependence of mean grain size and its variation with growth current. Our DF images indicate that the carbonaceous overcoat enveloping all nanowires possess an amorphous structure, Fig. 4. Moreover, as-grown W nanowires comprise nanosized grains with average size and size uniformity generally increasing with growth current. This phenomenon was accounted for by considering the nanocrystals are either irregularly shaped or columnar. Our observation that some grains have size smaller than the W core diameter also lead us to suspect that multiple grains may overlap across the W core region. Such speculation was confirmed via high resolution TEM imaging that aims to study the inner lattice structure of the specimens, Fig. 5. Moiré fringes arising from interference of periodic, non-parallel lattice fringes (grains) are frequently found in nanowires grown at or above 100nA, Fig. 5(a). For nanowires grown at and below 50nA, however, Moiré fringes are rarely observed suggesting enhanced probability of a single grain spanning across the W core diameter, Fig. 5(b). This observation implies a minimum attainable grain size for tungsten nanowire field-emission grown at room temperature. This may explain the general decrease in grain size variation as growth current decrease. Attempts to ascertain the absence of C within the nanowires by oxidatively removing the C overcoat in situ are currently underway.

References

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Figure 1: Indexed selected-area diffraction pattern for field-emission grown W nanowires based on PDF no. 04-0806.

Figure 2: (a) TEM bright-field image of a nanowire grown at 500nA. (b) EELS image constituted by energy-loss electrons of C revealing the carbonaceous nature of outer coat of a nanowire grown at 500nA. Same phenomenon was observed for all nanowires regardless of growth current.

Figure 3: A TEM dark field image typical of tungsten nanowires grown by cold field-emission showing their polycrystalline nature. An amorphous carbonaceous overcoat is evident on the exterior of the wire.

Figure 4: Plots of average diameter of tungsten (W) core □ and thickness of carbonaceous overcoat ▲ of as-grown nanowires versus field emission current. The average diameter of specimen grown at 1000nA varies from 5nm to 116nm and is not shown.

Figure 5(a): A typical high-resolution image of single W nanowires field-emission grown at or above 500nA with clearly visible Moiré fringes (circled). Inset (width: 4.8 nm) depicts lattice and Moiré fringes of as-grown nanowires.

Figure 5(b): A typical high-resolution image of single W nanowires grown at or below 100nA with periodic lattice fringes evidently shown. Moiré fringes, however, are relatively rare compared to Figure 5(a).