Characterisation of tungsten nano-wires prepared by electron and ion beam induced chemical vapour deposition.

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Abstract: In this study we present a morphological characterisation of tungsten nano-wires prepared by electron and ion beam induced chemical vapour deposition. Our observations show that both electron and ion beam as-deposited nano-wires exhibit an amorphous like microstructure. Irradiation of the electron beam deposited wires with 200kV incident electrons in the TEM was found to cause an electron beam induced anneal resulting in the formation of a localised nano-crystalline structure. Wires deposited using 30kV Ga⁺ ions were found to exhibit the appearance of low temperature superconducting properties with a critical transition temperature $T_c$ of ~5K.

1. Introduction

The direct fabrication of nano-structures or the modification of existing structures using focused ion or electron beams has attracted significant interest in recent years. Such a technique offers the means to rapidly develop nano-scale devices in a single processing step in-situ with no need for time consuming mask fabrication or extensive prior preparation of the sample. The ability to remove and deposit material with a high precision provides the ideal tool for the rapid prototyping of a whole range of devices in areas such as: quantum information processing, micro-electro-mechanical systems and optical applications [1]. Beam induced chemical vapour deposition (CVD) can be used to directly write patterns of metal, semi-conductor or insulator into a desired two or three-dimensional shape. The process involves the introduction of a precursor gas that contains the desired material to the vacuum chamber. The gas is introduced through a capillary needle in the vicinity of the focused beam and is absorbed onto the surface of the sample. As the beam is scanned over the surface of the sample in the desired pattern the precursor is decomposed into volatile and non-volatile components. The non-volatile component is deposited on the sample surface whilst the volatile product is removed via the instruments vacuum system. As part of a wider study to investigate the potential of focused beam induced CVD for the fabrication of novel electronic devices we report the deposition and characterisation of free standing tungsten nano-wires. In this study, we have applied high resolution TEM, micro-diffraction, energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) to characterise the morphology and composition of a series of tungsten wires prepared by ion and electron beam induced CVD denoted IBICVD and EBICVD respectively. We
also include the initial findings of our electrical characterisation which show the appearance of superconductivity in the wires deposited by IBICVD.

2. Experimental

Tungsten wires were grown in a JEOL 6500 FEGSEM fitted with an Orsay-Physics focussed ion column incorporating a liquid Ga⁺ ion source operating at 30 kV. The wires prepared for subsequent analysis in the TEM were deposited from the edge of the holes in a standard holey carbon film supported on a Cu grid. Deposition was achieved by use of a tungsten hexacarbonyl WCO₆ precursor gas which was bled into the specimen chamber via a capillary system to maintain a chamber pressure of 1-2×10⁻⁵ mbar. For IBICVD a dedicated Orsay-Physics software was utilised with a probe current of ~20pA and a beam scan frequency of 20000Hz. Ion beam deposited wires for electrical characterisation were deposited in a four-probe arrangement [2] using the same parameters but onto a SiO₂ substrate previously patterned with a series of gold interconnects and contact pads. Low temperature electrical measurements were performed in an Oxford Instruments liquid helium cryostat capable of reaching 1.6K. Control of the electron beam for EBICVD was achieved using the surface-editor module within the RAITH ELPHY Quantum Universal SEM/FIB Nanolithography System software. In the current study the field-emission electron source was operated at an accelerating voltage of 15kV with a corresponding probe current of ~ 250pA. Structural characterisation and microanalysis was performed in a JEOL 2010F field emission gun transmission electron microscope (FEGTEM) operating at 200kV. Compositional analysis was assessed using x-ray energy-dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). EEL spectra were recorded between zero and 700eV in image couple mode using an energy dispersion of 0.5eV/pixel. The imaging conditions were such to give a current density at the specimen of ~32A/cm². To assess the susceptibility of the wires to irradiation damage in the TEM imaging, experiments were performed at both ambient and liquid nitrogen temperatures.

3. Results and Discussion

Examples of wires grown by Ga⁺ ion beam and electron beam induced deposition are illustrated in figures 1a and 1b respectively. In both cases the microstructure shows no obvious long range order implying the as deposited material exists in an amorphous like state. The corresponding electron diffraction patterns are shown in the inserts. Although there appears to be little difference between the HREM images, the diffraction pattern from the ion beam induced wire shows a number of prominent features not observed in the EBICVD wire for the same imaging conditions. The pattern from the IBICVD wires exhibited an intense broad ring at 4.0-4.5nm⁻¹ with less intense broad halos at 7.7-8.3nm⁻¹ and 12.0-12.8nm⁻¹. No such reflections were observed in a diffraction pattern obtained from the adjacent amorphous carbon film which shows a diffuse halo around 2.4nm⁻¹.

![Figure 1](image_url). Nano-wires prepared by (a) IBICVD and (b) EBICVD. In both figures the inserts show the corresponding selected area electron diffraction pattern.
Hoyle et al [3] have reported similar observations in EBICVD deposited with a high beam dose in excess of 500C/m². It was suggested that the microstructure of such deposits were borderline between the amorphous and polycrystalline state but with a very small crystallite size. From our own observations we can conclude that if this is the case the crystallite size must be on a sub-nanometre scale. On the other hand, our EBICVD wires were found to only exhibit a weak broad reflection around 3.7-4.0nm⁻¹ suggesting a higher degree of disorder within the microstructure compared with the IBICVD wires.

The typical composition of IBICVD tungsten has been reported previously to be around 40, 40 and 20 atomic % for W, C and Ga respectively [4], the Ga being incorporated from the incident ion beam. These values are roughly consistent with our current observations with the addition of a small amount of oxygen in all the IBICVD wires studied. This is in contrast to the EBICVD wires which had a typical composition of 24, 40 and 36 atomic % W, C and O respectively. Obviously there is no Ga present in the EBICVD wires but the striking difference is the oxygen content. The relative C and O concentrations were derived from examination of the corresponding C and O K-edge EEL spectra. IBICVD wires typically gave C:O ratios between 1:0.03 and 1:0.1 whereas EBICVD wires gave values between 1:0.89 and 1:0.91. The relative EELS data is given in figure 2(a). In addition, all the wires examined in the TEM were found to be associated with a thin amorphous layer. EEL analysis of this layer confirmed the composition to be carbon only, likely derived from free carbon residues on the specimen surface migrating along the wires under the influence of the imaging beam.

Bulk Tungsten has a resistivity of 5 μΩ cm and Tungsten Carbide has a resistivity of 0.8 μΩ cm. However, as a consequence of the various impurities, material deposited by IBICVD has been shown to have a resistivity of around 200 μΩ cm while material prepared by EBICVD show a significant range in the resistivity, with values between 600 and 200,000 μΩ cm [3, 5-7]. It is generally acknowledged that the large variation in the resistivity of the deposited material is a consequence of differences in the deposition parameters. This is particularly so for EBICVD, where it has been reported that increasing the probe current, or decreasing the energy, of the incident electron beam has the effect of producing material with a lower resistivity [5,6]. In the current study, the measured room temperature resistivity for nano-wires prepared by 30kV Ga⁺ ion and 15kV electron beam induced deposition were 140 and 10,000 μΩ cm respectively. It is known that amorphous W films show interesting superconducting properties at low temperature [8]. We too have observed the appearance of low temperature superconductivity at ~5.0 K in nano-wires prepared by IBICVD as shown in figure 2(b). These findings are consistent with the very recent reports on similar materials by Sadki et al [4].

![Figure 2](image-url)  
**Figure 2.** (a) EELS spectra showing the relative carbon and oxygen K edge signal from (i) EBICVD wire, (ii) IBICVD wire and (iii) From the amorphous region at the periphery of the wires. (b) Low temperature electrical characteristics showing the appearance of superconducting properties ~5K.
The EBICVD wires in contrast, did not show any evidence of low temperature superconductive properties (the full characterisation of which will be reported elsewhere).

The susceptibility of the as deposited nanowires to irradiation with 200kV electrons in the TEM was also assessed. In this study, the ion beam deposited wires were found to show reasonable stability under the electron beam with little or no change of the microstructure even after prolonged periods of illumination with highly focused probes. On the other hand, the electron beam deposited wires were prone to damage under relatively moderate electron flux densities. Figure 3 shows a HREM image of a typical EDICVD wire after exposure to continuous electron illumination with a current density at the specimen of ~32A/cm² for 8 minutes. A beam induced reorganisation of the microstructure has clearly occurred with the previously as deposited amorphous like structure now exhibiting lattice fringes corresponding to the formation of 2-3nm poly-crystals. Corresponding observations at liquid nitrogen temperature revealed that the rate of re-crystallisation was significantly retarded. This implies that the dominant damage mechanism in this case may be that of localised electron beam induced heating. Further studies on the stability of the W nano-wires discussed in this report are currently underway.

4. Conclusions
Morphological characterisation of tungsten nano-wires prepared by electron and ion beam induced CVD show the microstructure of the as-deposited nano-wires to be predominantly amorphous-like. However, some evidence of a sub-nanometre short range order was indicated from electron diffraction studies. Exposure of the EBICVD wires to 200kV incident electrons in the TEM was found to induce a localised anneal of the wire resulting in the formation of a nano-polycrystalline structure. Room temperature resistivity for the ion and electron beam induced CVD wires were 140 and 10,000 µΩ cm respectively. The appearance of superconducting properties in the wires deposited using 30kV Ga⁺ ions was observed with a critical transition temperature Tc of ~5K.

5. References
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