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Growth and characterization of tungsten carbide nanowires by thermal annealing of sputter-deposited WC<sub>x</sub> films

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In this letter, the growth of dense W<sub>2</sub>C nanowires by a simple thermal annealing of sputter-deposited WC<sub>x</sub> films in nitrogen ambient is reported. Straight nanowires with a density of 250–260 µm<sup>−2</sup> and length/diameter in the range of 0.2–0.3 µm/13–15 nm were obtained from the 700°C-annealed samples, which exhibit good electron field emission characteristics with a typical turn-on field of about 1.7 V/µm. The self-catalytic growth of W<sub>2</sub>C nanowires is attributed to the formation of α-W<sub>2</sub>C phase caused by carbon depletion in the WC<sub>x</sub> films during thermal annealing. © 2004 American Institute of Physics. [DOI: 10.1063/1.1791322]

Electron field emission (FE) from durable emitter materials has received much attention due to their potential applications as cold cathodes in flat panel display and nanoelectronics. Though researchers are still actively looking for alternative materials, diamonds, diamond-like carbon, amorphous carbon, carbon nanotubes (CNTs), etc., have been widely studied as possible candidates for FE emitters. In general, a qualified material used as FE emitter should be made of highly conductive film with high mechanical strength, high emission site density, high thermal conductivity, and low FE threshold fields.

Refractory metal carbides (RMCs), such as TaC, TiC, WC, etc., have been applied as diffusion barrier layers in Al and Cu metallization due to their good electrical conductivity, high chemical inertness, and low atomic diffusion at high temperatures. It is expected that the growth of nanosized structures from RMC films, if possible, would be beneficial to the improvement of electron FE properties for actual device performance. However, there have been very limited reports on the electron field emission of RMC films. In this letter, we report on the growth of tungsten carbide nanowires by a simple thermal annealing of sputter-deposited WC<sub>x</sub> films. The self-catalytic growth behavior and microstructures of the thermally annealed WC<sub>x</sub> films were investigated. FE properties of the nanowires were examined. Through material and structural analysis, a possible self-catalytic growth mechanism is proposed.

In experiments, WC<sub>x</sub> films with thickness in the range of 15–60 nm were sputter-deposited on n-type Si(100), 10 Ω cm substrates. A dc magnetron sputtering system using a water-cooled WC target (50.50 wt %) with 99.5% purity was used. The deposition was carried out under an argon flow rate of 24 sccm, a dc power of 200 W, and a pressure of 7.6 m Torr at room temperature. The typical deposition rate was measured to be around 0.36 Å/s. The as-deposited samples were subsequently subjected to thermal annealing in quartz tube furnace with a temperature ranging from 600 to 850°C in N<sub>2</sub> ambient for 30 min.

Figure 1 shows the typical scanning electron microscopy (SEM) image for the 700°C-annealed sample and insets of the figure for the 650 and 750°C-annealed samples. All samples are with 60 nm in thickness. Similar results were also found on samples with other thicknesses. It is seen that nanosized white protrusions appear on the surface of the 650°C-annealed samples, while samples annealed at lower temperatures (≤600°C) show a smooth and clean surface. After thermal annealing at 700°C, the small extrusions have developed into dense and randomly oriented nanowires with a density of 250–260 µm<sup>−2</sup>. After annealing at 750°C, however, most of the nanowires have been transformed into dark-colored grains with a typical size of 6.8–7.5 × 10<sup>−3</sup> µm<sup>2</sup>. Upon further increasing of the annealing temperatures to 800 or 850°C (not shown), the grain size was enlarged and a relatively smoother surface appeared.

Figure 2 presents the transmission electron microscopy (TEM) image of the nanowires synthesized on the 700°C-annealed samples. Essentially, the nanowires are all with a straight body. The typical diameter and length of the nanowires are of 13–15 nm and 0.2–0.3 µm, respectively. Also shown in the inset to Fig. 2 is the selected area diffraction (SAD) pattern for an individual nanowire. The inner and outer rings indicated by an arrow are with a d space of 2.36 and 1.35 Å, which corresponds to the phase of α-W<sub>2</sub>C.

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W₂C(002) and α-W₂C(103), respectively. Between the above two rings, WO₃(220) with d space of about 1.72–1.73 Å was observed. As compared to tungsten (W) nanowires synthesized from pure W films reported by Lee et al., the W₂C nanowires have a much higher density than that of W nanowires, in addition, the temperature required for the growth of W₂C nanowires is around 700°C, which is about 150°C lower than that used in their work.

The FE characteristics of the WCₙ nanowires were measured in a parallel plate configuration with a gap spacing of 210 μm and a contact area of 1.5 x 10⁻² cm² at a pressure of 1 x 10⁻³ Torr. Since the WCₙ films are highly conductive with a typical resistivity of 200–230 μΩ cm as measured by four-point probe technique, essentially, the FE characteristics of the prepared samples are not sensitive to the film thickness in the range of 15–60 nm. Figure 3 illustrates the typical Fowler–Nordheim (FN) ln(J/E²) versus (1/E) plots for the WCₙ films annealed at 650 and 700°C. Samples annealed at 750 and 800°C show poor FE properties. The linear FN characteristics indicated that electron emission of W₂C nanowires should be dominated by the FN process. According to the FN model⁶ and assuming a work function of 4.5–5.0 eV, the extracted enhancement factors β for the 650 and 700°C-annealed samples are of 4267–4998 and 5413–6339, respectively. Though these values are comparable higher than some reported values for CNTs, to further improve FE properties, efforts including additional treatment to achieve alignment and elongating the length of the nanowires for FE applications are still necessary. The turn-on field at an emission current density of 1 μA/cm² for the 650 and 700°C-annealed samples is about 2.1 and 1.7 V/μm, respectively.

Figure 4 is a typical x-ray diffraction (XRD) pattern of the prepared samples, taken with a Rigaku D/MA2500 diffractometer at a scan step of 0.01°, using Cu Kα (wavelength of 1.5418 Å) radiation. For the as-deposited sample, a single broad peak corresponding to WCₙ phase was observed. After thermal annealing at 600 and 650°C, the peak was seen to shift to a value of 38.03° corresponding to WCₙ(002) phase. The XRD spectra for the 700°C-annealed WCₙ films were seen to be dominated by the α-W₂C and WCₙ phases. The appearance of WCₙ phase was decomposed and carbon depletion together with the formation of α-W₂C structure occurred. The same phenomenon has been reported by Romanus et al.⁶⁰ With increasing the annealing temperature to 700°C, the original α-W₂C peak was observed to broaden and get an asymmetrical shape. This anomalous peak can be deconvoluted into six Gaussian peaks corresponding to WCₙ, WO₂, W₅Si₃, β-W, and α-W phases. The XRD patterns for the 750, 800, and 850°C-annealed samples, the intensity of α-W₂C and β-W peak is seen to decrease with increasing annealing temperature, while the intensity of α-W peak exhibits a reverse situation. It is noted that samples annealed at 700°C and above show a significant portion of W₅Si₃(321) phase. However,
as revealed by AES depth profiles (not shown), no sign of Si appears on the surface and the W$_3$Si$_3$ phase only accumulates at the WC$_x$/Si interface. The influence of W$_3$Si$_3$ phase on nanowire formation is limited.

As reflected from XRD analysis, thermal annealing has rendered the main structure of the WC$_x$ films undergoing a sequential change from WC$_x$ phase ($<$600°C) to α-W$_2$C (~600–700°C), to β-W (~700–800°C), and finally, to α-W phase (~800 and 850°C). Judging from SEM images the onset of the appearance of nanostructures at 650°C, the growth of dense nanowires at 700°C, and the disappearance of nanowires at 750–800°C, it is very interesting to find that this trend was parallel to the variation of the intensity of the α-W$_2$C (002) peak as revealed by XRD analysis. Obviously, carbon plays an important role in the growth and collapse of nanowires on annealed WC$_x$ films.

The self-catalytic growth of W$_2$C nanowires should be attributed to the formation of α-W$_2$C structures caused by carbon depletion in the WC$_x$ films during thermal annealing. In addition, the collapse of W$_2$C nanowires in samples annealed at temperatures ≥700°C is due to the nanowires experiencing a structure transformation from α-W$_2$C (002) phase into grains of β-W phase.

In conclusion, self-catalytic synthesis of W$_2$C nanowires from a simple thermal annealing of sputter-deposited WC$_x$ films in N$_2$ ambient and their FE properties have been reported. Dense W$_2$C nanowires with a typical diameter and length of 13–15 nm and 0.2–0.3 µm, respectively, have been obtained from the 700°C-annealed WC$_x$ films, which exhibit good FE properties with a turn-on field of 1.7 V/µm. According to material analysis, the possible mechanism governing the self-catalytic growth of W$_2$C nanowires should be attributed to the phase change from WC$_x$ to W$_2$C during thermal annealing. The low turn-on field paired with high packing density and simple growth process indicates that W$_2$C nanowire could be a potential material for field emitters.

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