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Growth and characterization of tungsten carbide nanowires by thermal annealing of sputter-deposited WC_x films

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In this letter, the growth of dense W_2C nanowires by a simple thermal annealing of sputter-deposited WC_x films in nitrogen ambient is reported. Straight nanowires with a density of 250–260 μm^{-2} 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_2C nanowires is attributed to the formation of α-W_2C phase caused by carbon depletion in the WC_x 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,[1] diamond-like carbon,[2,3] amorphous carbon,[4,5] carbon nanotubes (CNTs),[6,7] etc., have been widely studied as possible candidates for FE emitters.[8] 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.[9,10]

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.[11–14] 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.[8,15] In this letter, we report on the growth of tungsten carbide nanowires by a simple thermal annealing of sputter-deposited WC_x films. The self-catalytic growth behavior and microstructures of the thermally annealed WC_x 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_x 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_2 ambient for 30 min.

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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^{-2}. 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^{-3} μm^2. 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-

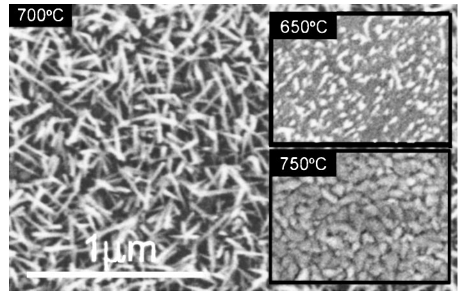

FIG. 1. Top view SEM image of the 700 °C-annealed WC_x films. Insets are the SEM images of samples annealed at 650 and 750 °C. The scale bar is applied to all figures. Thermal annealing was performed in N_2 ambient for 30 min.

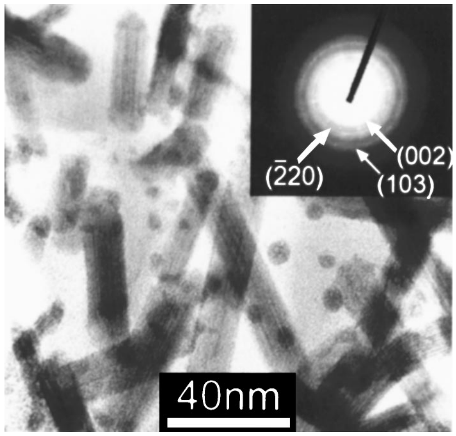

FIG. 2. TEM images of W_2C nanowires obtained from the 700 °C-annealed samples. Inset is the SAD diffraction pattern for individual nanowires.

$W_2C(002)$ and α-$W_2C(103)$, respectively. Between the above two rings, $WO_2(\overline{2}20)$ 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.*,[15] the W_2C nanowires have a much higher density than that of W nanowires, in addition, the temperature required for the growth of W_2C nanowires is around 700 °C, which is about 150 °C lower than that used in their work.

The FE characteristics of the WC_x nanowires were measured in a parallel plate configuration with a gap spacing of 210 μm and a contact area of 1.5×10^{-2} cm^2 at a pressure of 1×10^{-7} Torr. Since the WC_x films are highly conductive with a typical resistivity of 200–230 $\mu\Omega$ 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) $\ln(J/E^2)$ versus $(1/E)$ plots for the WC_x 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 W_2C nanowires should be dominated by the FN process. According to the FN model[16] and assuming a work function of 4.5–5.0 eV,[15,17,18] 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 comparably higher than some reported values for CNTs,[18,19] to further improve FE properties, efforts including additional

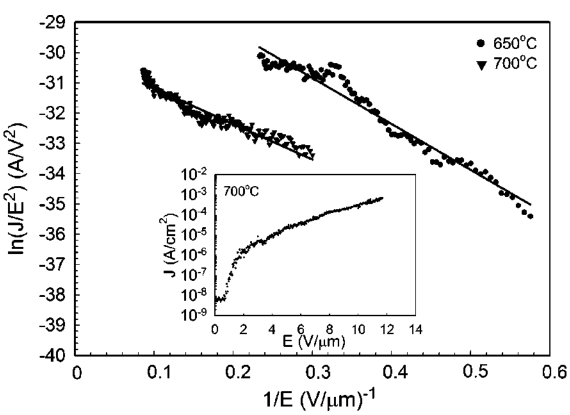

FIG. 3. The Fowler Nordheim (FN) plots for the 650 and 700 °C-annealed films. The inset shows the typical *I-V* curve for the 700 °C-annealed samples.

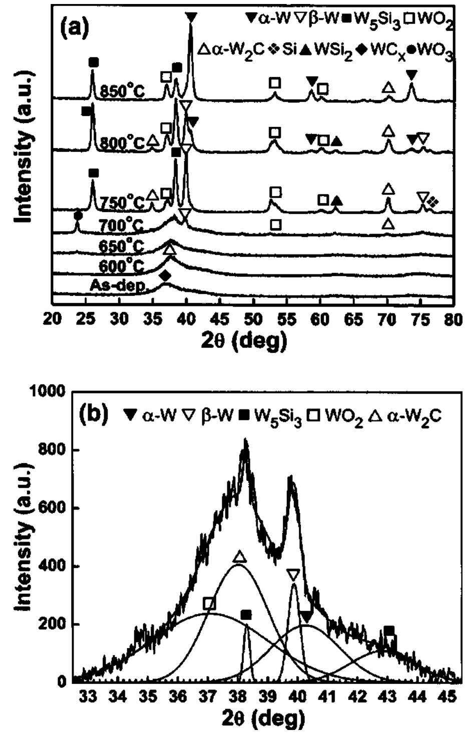

FIG. 4. (a) XRD patterns of the as-deposited and annealed WC_x films. (b) XRD spectra of the 700 °C-annealed WC_x film in the range of 33°–45°. This anomalous peak has been deconvoluted into six Gaussian peaks corresponding to W_2C, WO_2, W_5Si_3, β-W, and α-W phases.

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/cm^2 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/MAX2500 diffractometer at a scan step of 0.01°, using Cu $K\alpha$ (wavelength of 1.5418 Å) radiation. For the as-deposited sample, a single broad peak corresponding to WC_x 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 the α-W_2C (002) phase. It indicates that a finite amount of carbon was decomposed and carbon depletion together with the formation of α-W_2C structure occurred. The same phenomenon has been reported by Romanus *et al.*[20] With increasing the annealing temperature to 700 °C, the original α-W_2C peak was observed to broaden and get an asymmetrical shape. This anomalous peak can be deconvoluted into six Gaussian peaks as shown in Fig. 4(b). Note that the main peak centered at ~38.03° corresponds to α-W_2C (002), while the other peaks correspond to WO_2, W_5Si_3, β-W, and α-W phases. The appearance of β-W and α-W phases indicates that a further amount of carbon depletion occurred in the 700 °C-annealed films. Further increasing the annealing temperature above 700 °C, the main structure of the annealed films was seen to be dominated by β-W and then by α-W phase. Comparing the XRD patterns for the 750, 800, and 850 °C-annealed samples, the intensity of α-W_2C 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 W_5Si_3 (321) phase. However, as revealed by AES depth profiles (not shown), no sign of Si appears on the surface and the W_5Si_3 phase only accumulates at the WC_x/Si interface. The influence of W_5Si_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_2C ($\sim 600-700\,°C$), to β-W ($\sim 700-800\,°C$), 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_2C (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_2C nanowires should be attributed to the formation of α-W_2C structures caused by carbon depletion in the WC_x films during thermal annealing. In addition, the collapse of W_2C nanowires in samples annealed at temperatures $\geqslant 700\,°C$ is due to the nanowires experiencing a structure transformation from α-W_2C (002) phase into grains of β-W phase.

In conclusion, self-catalytic synthesis of W_2C 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_2C 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_2C nanowires should be attributed to the phase change from WC_x to W_2C during thermal annealing. The low turn-on field paired with high packing density and simple growth process indicates that W_2C nanowire could be a potential material for field emitters.

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