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The Influence of Carbon Content on Material and Field Emission Properties of Nanowires Self-synthesized from Sputter-deposited WC_x Films

Rong-Ming Ko, Shui-Jinn Wang*, Chao-Hsuing Chen, Wei-Chih Tsai, Yi-Cheng Kuo, Chia-Lung Chang, and Zhi-fu Wen

Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan, Republic of China
*Phone: +886-6-2757575-62351 E-mail: sjwang@mail.ncku.edu.tw

1. Introduction

Nanoscale materials, such as nanotubes, nanowires, nanobelts, and nanorods have attracted lots of attention because they exhibit many superior properties as compared to bulk materials. Recently, the self-growth of tungsten carbide (W_2C) nanowires by a simple thermal annealing and tungsten oxide ($W_{18}O_{49}$) nanowires by a annealing/oxidation process from sputter-deposited tungsten (W)-based films (W and WC_x) has been reported by the authors' group [1-4]. Due to its outstanding field emission characteristics, the developments of W-based nanowires are expected to open a new era in the applications of field emitters for flat panel displays (FPDs) and general lighting in the near future.

In general, field emission (FE) properties of nano-structured emitters have been found strongly depending on the density and size of the nanowires [5]. The emitted current density can be optimized by tuning the density and size of nanowires to minimize the electric field screening effect [5, 6]. In this work, the influence of the carbon content in the WC_x sputtering target on the density, shape, and nanostructure of the self-growth W-based nanowires was investigated. The physical insights of carbon content in governing the self-growth of nanowires, especially on their growing density and size, were investigated. Finally, the optimal carbon content for the self-growth of W-based nanowires with superior field emission performance was also proposed.

2. Experiment

In experiments, a sputtering system using three water-cooled W-based targets (W:C ratios of 100:0, 95:5, 70:30, all in wt%) with 99.5% purity was used. The deposition was carried out under an argon flow rate of 24 sccm, a dc power of 100-200 W, and a pressure of 7.6 m Torr at room temperature. The typical deposition rate was measured to be in the range of 0.15-0.33 Å/s. Pure W and WC_x films with thickness of about 60 nm were sputter-deposited on n-type Si (100), 1-10 Ω cm substrates. After deposition, these samples were subjected to thermal annealing in a quartz tube furnace with a temperature ranging from 650 to 850°C in N_2 ambient for 30 min for the growth of nanowires.

3. Results and Discussion

Figure 1 shows the SEM images of the prepared samples after thermal annealing at 650-750°C in N_2 ambient for 30 min. Densities, diameter, and length of nanowires estimated from SEM images of the 650-, 700-, and 750 °C-annealed samples were summarized in Table 1. For samples annealed at the same condition, the size of nanowires is seen increasing with the carbon content. It is noted that the dimension of nanowires significantly increases with increasing the annealing temperature, while the density of nanowires has an inverse situation. Our results suggest that tailoring both density and geometry of nanowires for better FE properties would be possible through suitable adjusting the carbon content and annealing conditions.

Table 1 Summary of the density, diameter, and length of nanowires self-synthesized from the deposited films with different carbon content.

Annealing Temp. (°C)	W:C (wt%) of deposited films		
	100:0*	95:5*	70:30*
650	720/20/0.05	320/17/0.10	356/17/0.13
700	424/23/0.11	188/17/0.16	256/20/0.21
750	336/27/0.16	140/20/0.21	152/23/0.40

*Unit: density (μm^{-2})/diameter (nm)/and length (μm)

Figure 2 shows the TEM images of a single nanowire obtained from the sputter-deposited pure W film after thermal annealing at 700°C for 30 min. Similar TEM images of nanowires were also obtained from the other two WC_x films (not shown). The diameter and length of the wire was about 23 nm and 0.2 μm, respectively. Inserts (a) and (b) are the typical SAED patterns for a single nanowire obtained from the pure W and the WC_x (W:C=70:30 wt%) film, respectively. For pure W films, the d space of grown nanowires was determined to be 3.78 Å and the crystallization phase could be identified as the non-stoichiometric monoclinic $W_{18}O_{49}$ (010). While for nanowires obtained from the (W:C=70:30 wt%)-films, an additional ring of W_2C (002) was seen in SAED and its d space was 2.36 Å. It indicated

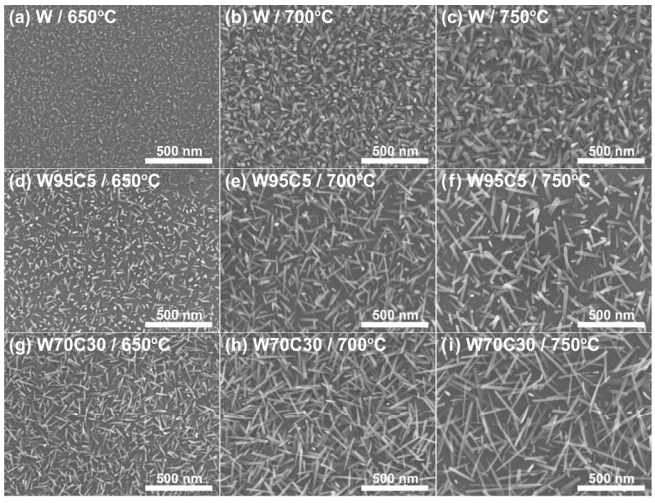

Fig. 1 Top view SEM images of the 650-, 700-, and 750°C-annealed pure W, WC (95:5 wt%), and WC (70:30 wt%) films. Thermal annealing was performed in N_2 ambient for 30 min.

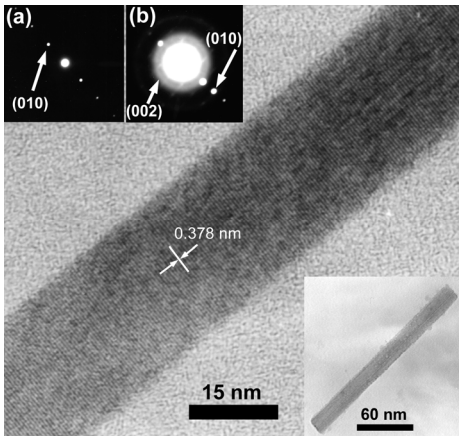

Fig. 2 Typical TEM images of nanowires obtained from the sputter-deposited pure W film after thermal annealing at 700°C for 30 min. Inserts are the typical SAED patterns for a single nanowire obtained from the pure W and the (W:C=70:30 wt%) film, respectively.

these nanowires mainly comprising of multiple phases of $W_{18}O_{49}$ (010) and W_2C (002) nano-crystallization. Obviously, the carbon content of thin films leads to the self-synthesis of an additional W_2C phase in nanowires.

Figure 3 shows the XRD analysis of annealed samples. For the pure-W film, the peak at around 23.4-23.5° ($W_{18}O_{49}$ (010)) is seen. This peak was also observed from the other two films but with its intensity decreases with increasing the carbon content. Moreover, an inverse situation was found for the peak of WO_2/W_2C nano-crystallization. This result indicates that the amount of WC_x phase appearing in the annealed films or nanowires increases with increasing the carbon content, which is in good agreement with the result of SAED analysis.

Figure 4 illustrates the typical Fowler-Nordheim (FN) plot of samples. The linear FN characteristics indicated the electron emission of tungsten based nanowires should be dominated by the FN process. According to FN tunneling current equation ($J = C_1(\beta E)^2 e^{-(C_2\phi^{3/2}/\beta E)}$) and using a value of 5 and 4.63 eV for the work function (ϕ) of W and WC_x films, respectively, an enhancement factor (β) as high as 5570 was obtained from nanowires self-grown on WC (70:30 wt%) films. The corrresponding J-E plot (inset) indicates a low turn-on (E_{on}) field of about 1.4 V/μm. In addition, for samples of WC (95:5 wt%), the poor emission property might be attributed to its relatively low density of nanowires as compared to samples of pure W, and its relatively low growing aspect ratio for nanowires as compared to samples of WC (70:30 wt%).

4. Conclusions

The influence of carbon content on both material and field emission properties of W-based nanowires self-synthesized from WC_x films has been investigated. It has been found that the size of nanowires could be enhanced by increasing the carbon content, in addition, relatively better field emission property with a turn-on field as low as 1.4 V/μm was obtained for nanowires prepared from WC (70:30 wt%) films. It is expected that, through the control of carbon content in the sputtering target and thermal annealing conditions, W-based nanowires with desired diameter, length, and

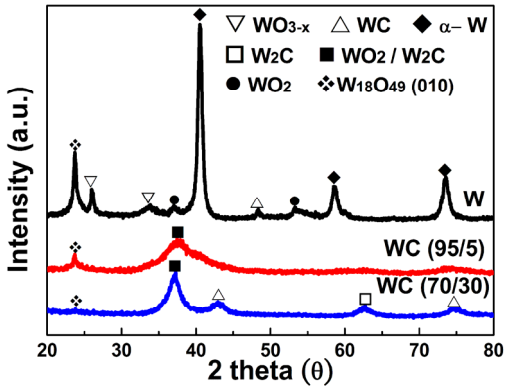

Fig. 3 XRD patterns of the 700°C-annealed W and WC_x films.

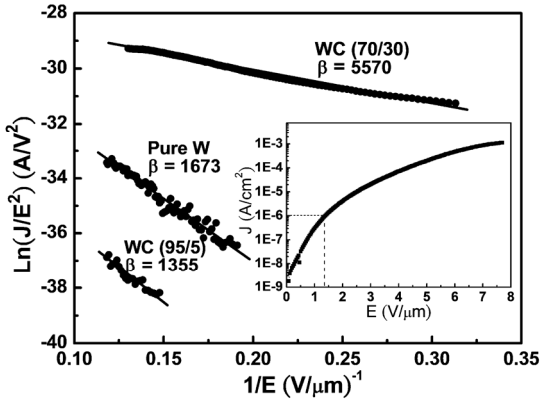

Fig. 4 The Fowler-Nordheim (FN) plots for nanowires obtained from W and WC_x films with different carbon content after annealed at 750°C for 30 min. The inset shows the typical J-E curve for nanowires prepared from WC (70:30 wt%) samples.

density for achieving superior FE characteristics for field emission displays (FEDs) and general lightings would be very possible.

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