MULTISECTIONAL SYNTHESIS OF TUNGSTEN OXIDE NANOWIRES USING MICROPATTERNED LAYER FOR FIELD-EMISSION DISPLAYS

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INTRODUCTION
Tungsten oxide nanowires (Figure 1(a)) are one-dimensional nanostructures, with diameters of 10-100 nm and a length of about 1 μm. The nanowires are spontaneously grown by the simple annealing of pure tungsten materials up to about 800 °C. Since the nanowires have high aspect ratios and are easily fabricated, they have attracted considerable attention as promising materials for field emitters of field-emission displays (FEDs) [1-3]. However, since the nanowires grow randomly, field emission is not uniform in a pixel (Figure 1(b)) [4]. Therefore, it is necessary to control the growth section in order to utilize the nanowires for FEDs. Moreover, heating the entire system for the synthesis of the nanowires may damage the system. To resolve these problems, multisectional heating has been attracting considerable attention. We proposed a new multisectional heating process using a micropatterned layer and local current heating (Figure 2).

MULTISECTIONAL HEATING USING MICROPATTERNED LAYER AND LOCAL CURRENT HEATING
We used W/Cr films sputtered with thicknesses of 200/50 nm on Si substrates covered with an oxide layer (SiO₂) as samples. The thickness of the SiO₂ layer was 1 μm. These films were deposited by standard radio frequency magnetron sputtering. The Cr film prevented the W film from detaching from the Si substrates. Ar was used as sputtering gas. The base pressure of the sputtering chamber was 1 × 10⁻² Pa and the sputtering pressure was 5 × 10⁻¹ Pa. The deposition rate of tungsten was 13 nm/min. After deposition, we covered each sample with a positive photoresist (AZ-1500 (20cP), AZ Electronic Materials) using a spin coater. The thickness of the photoresist was 1 μm. Each sample was exposed to ultraviolet light through a photomask with the pattern of the micropatterned layer. The photoresist exposed was removed using a photoresist developer and the W/Cr film was etched using etchants. After etching, the photoresist that remained on the pattern was removed using a photoresist remover.

FIGURE 1. (a) SEM image of tungsten oxide nanowires. (b) Fluorescence image of field emission through phosphor-coated ITO glass and tungsten film with tungsten oxide nanowires.
To date, we have successfully synthesized tungsten oxide nanowires simultaneously on a regular 20 by 20 array of narrow sections with a pitch of 15 μm using the micropatterned layer (Figures 3(a-d)) [5]. This synthesis required a voltage of 19 V and a current of 0.49 A. The vacuum chamber maintained an oxygen atmosphere of 4 × 10^{-2} Pa.

Figure 4 shows a schematic of the application of the multisectional synthesis of tungsten oxide nanowires for manufacturing FEDs. The regions of the nanowires are controlled in a pixel by the micropatterned layer. Moreover, by using the micropatterned layer as the lower electrode of a display, wiring systems are not required.

**RELATIONSHIP BETWEEN DISPERSION DEGREE OF TUNGSTEN OXIDE NANOWIRES AND FIELD-EMISSION PROPERTIES**

Generally, the dispersion degree of the emitters significantly affects their field-emission properties for the concentration of the electric field (Figures 5(a-b)) [6, 7]. To realize FEDs with nanowires synthesized using local current heating, the dispersion of the synthesis sections must be optimized. As a preliminary experiment, we studied the relationship between the dispersion degree of the nanowires and the field-emission properties.

In this study, we developed islandlike patterns of W/Cr films to disperse the nanowires deliberately (Figure 6). We varied the dispersion degree of the nanowires by varying the pitch of the patterns. We synthesized the nanowires on each pattern using a vacuum furnace and investigated the conversion of their field-emission properties.
FIGURE 5. Schematic of effect of dispersion degree of emitters on concentration of electric field. Emitters exist (a) uniformly and (b) dispersively.

FIGURE 6. Schematic of tungsten oxide nanowires synthesized on islandlike patterns of W/Cr films.

EXPERIMENTAL
We fabricated patterns of W/Cr films using a lift-off process. We covered a Si wafer with a positive electron beam (EB) resist (ZEP-520A, ZEON Corporation). The thickness of the resist was 400 nm. The wafer was exposed to EBs with a program to write the micropatterned layer. The EB resist exposed was removed using an EB resist developer. We sputtered W/Cr films on the wafer. The sputtering conditions were the same as those in the experiment using local current heating, except the deposition rate of 6 nm/min. After deposition, we lifted off the W/Cr films using toluene and a supersonic cleaner.

We developed four patterns in this experiment (Figures 7(a-d)). The pitches of 1 x 1 μm² squares were (a) 2, (b) 5, (c) 10, and (d) 15 μm. The patterned area was 5 x 5 mm². We annealed the samples in the vacuum furnace at a temperature of 560 °C by infrared heating, while controlling the oxygen pressure to 4 x 10⁻² Pa by introducing oxygen gas. The base pressure of the vacuum furnace was 3 x 10⁻³ Pa. To investigate the field-emission properties, the samples were set in a vacuum chamber through ITO glass and connected with a high voltage power supply (Figure 8). The gap of the samples and ITO glass was 50 μm. The base pressure of the vacuum chamber was 2 x 10⁻³ Pa.

FIGURE 7. SEM images of 1 x 1 μm² square patterns with pitches of (a) 2, (b) 5, (c) 10, and (d) 15 μm.

FIGURE 8. Schematic of field-emission experiment.

RESULTS AND DISCUSSION
Figure 9 shows the SEM image of one of the square patterns after annealing. Tungsten oxide nanowires were synthesized on the square patterns. The length of the nanowires was 100-500 nm, and the number of nanowires on one square was 60-80. Figure 10 shows the current density versus electric field (I-V) plot and Fowler-Nordheim (F-N) plot of the samples. In the sample with a pitch of 5 μm, current was first detected at an electric field of about 35 V/μm. In the samples with pitches of 10 and 15 μm, current was first detected at an electric field of 20-30 V/μm. The maximum current densities obtained immediately before discharging were 22 μA/cm² with a 5 μm pitch, 65 μA/cm² with a 10 μm pitch, and 82 μA/cm² with a 15 μm pitch. Generally, the longer the pitch, the better the field-emission properties. This tendency agrees with the general relationship
between the dispersion degree of the emitters and field-emission properties. If we use a pattern with a longer pitch, field-emission properties will become better. In the sample with a 2 μm pitch, electric discharging was observed before field emission.

CONCLUSION
We studied the relationship between the dispersion degree of tungsten oxide nanowires and field-emission properties. We used the nanowires synthesized on the patterns of W/Cr films as the samples. By varying the pitch of the patterns, we varied the dispersion degree of the nanowires. We observed that the sample with a long pitch resulted in better field-emission properties. In this technique, we can optimize the dispersion of the synthesis sections for local current heating.

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REFERENCES


