Chapter 9
Conclusions

In this study, ordered arrays of nanomaterials including carbon nanotubes (CNTs) and titanium oxide nanodots are successfully grown by using the nanopores of anodic aluminum oxide (AAO) films as templates. Nanoporous AAO films are prepared by the two-step anodization of aluminum films. The AAO template assisted CNT arrays are synthesized by microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD). Ordered nanodot arrays of titanium oxides are constructed by anodizing the Al/TiN bilayered films. The field emission characteristics as well as field emission device applications of the nanomaterials have been investigated. The primary results obtained in this dissertation are summarized as follows:

(a) Ordered nanopore arrays of the AAO films with 23-140 nm interpore distances have been prepared by the two-step anodization of thermal evaporated aluminum films coated on silicon substrates. The interpore distance increases linearly with anodic voltage. The pore arrangements show polycrystalline structures with ordered domains in the diameters of a few micrometers (short-range order).

(b) Vertically aligned and well-graphitized CNT arrays, in terms of the AAO templation, can be synthesized by using the microwave plasma ECR-CVD system. We ascribe the vertical alignment of the nanotubes to the AAO template effect and the dc bias as well as the plasma induced self-bias. The nanotube growth is catalyzed by the pre-deposited cobalt catalyst inside the nanopores and by means of the tip-growth mechanism. The nanotubes confined by the AAO nanopores are very uniform in diameter. The tube length can be reliably controlled via the growth time, which is essentially important to fabricate the triode devices using the CNT emitters. Field emission measurements reveal that the CNTs grown for 30 min (overgrown length: 700 nm-1.5 μm) show an emission current density as high as 95 mA/cm^2 at an applied electric field of about 8.5 V/μm and possess a significantly high value of the field enhancement factor of about 2600.

(c) The tube number density of CNTs grown over the nanoporous AAO template can be directly controlled by adjusting the CH_4:H_2 feed ratio during the CNT growth in the ECR-CVD. The variation of the tube number density as a function of the CH_4:H_2 feed ratio correlates with the kinetic competition between outgrowth of the cobalt-catalyzed CNTs from the AAO pore bottom and deposition of the amorphous carbon overlayer on the AAO template. The pore-filling ratio for the nanotubes overgrown out of the nanopores decreases from 82 to 18%, when the CH_4 concentration increases from 9 to 91%. Enhanced field emission properties of the CNTs are obtained by lowering the tube number density because of the alleviation of the field-screening effect. However, at a high CH_4 concentration, amorphous carbon byproduct would deposit on the CNT surface and degrade the field emission properties due to a high energy barrier and significant potential drop at the emission site.

(d) Self-organized nanodot arrays of titanium oxides are prepared from Al/TiN bilayered films by anodization of a TiN layer using a nanoporous AAO film as the template. The ordered nanodots can faithfully duplicate the shape and hexagonal arrangement of the AAO nanopores, and the dot size is adjustable depending on the anodization conditions. The shape uniformity of the nanodots can be effectively improved by using an epitaxial Al/TiN bilayered film on a sapphire substrate. After high temperature annealing, the nanodots are consisted of two dominant grains of anatase and rutile phases. Because the high temperature crystallization process is confined in the isolated dome structure, the grain growth and the anatase-to-rutile phase transition are retarded, resulting in the stable existence of the metastable anatase phase at high temperature (higher than 1200 ^{o}C).

(e) The self-organized nanodots with low fabrication cost and excellent uniformity over a large area compared with CVD process are promising candidates for field electron emitters. We have proposed a field emission triode device using the nanodot arrays as the emitters. The fabrication process is an easily controllable and integrated circuit (IC) technology compatible process. The high geometrical enhancement and excellent uniformity of the nanodots give the devices with a low gate turn-on voltage of 45 V and considerably high emission current density of 25 mA/cm^2 at 120 V.

Chapter 10

Future Prospects

We have shown that anodic aluminum oxide (AAO) is an ideal template material for preparing ordered arrays of carbon nanotubes (CNTs) and nanodots. The obtained nanomaterial arrays are highly promising for electron field emission applications. However, some subjects should be further studied:

(a) A systematic study of the temperature dependence of the AAO template assisted CNT growth in microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD) should be proceeded.

(b) Although the amorphous carbon byproduct can effectively decrease the tube number density of CNTs on the AAO template, it would interference the electron emitting behavior of CNTs. Nevertheless, it is expected that if only the CNT surface is cleaned up by post-growth treatment, such as hydrogen plasma treatment, the low tube number density provided field enhancement may be more highlighted.

(c) Some physical properties, such as photoluminescence (PL), photo-adsorption, electrical conductivity, etc., of the self-organized nanodots should be further studied, which is scientific importance and technological significance of future applications.

(d) According to thermodynamic calculations, we concluded that the titanium oxide (TiO_2) nanodots with a stable single phase of anatase can be accomplished when the dot size is smaller than a critical size. However, this prediction should be further verified by experimental data.

(e) Iridium dioxide (IrO_2) possesses higher electrical conductivity and lower surface work function compared with TiO_2. Therefore, the self-organized emitters based on IrO_2 nanodots may show better field emission property than the TiO_2 nanodots.