Chapter 1

Introduction

1.1 Introduction to nanomaterials

Nanomaterials are defined as that the materials have at least one dimensional within the scales from one nanometer to one hundred nanometers. In the past few years, the field of nanomaterials is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide. There are several reasons for this. One is the demand to fabricate new materials on an ever finer scale to continue decreasing the cost and increasing the speed of information transmission and storage. Another is that nanomaterials exhibit novel, size-dependent, and often enhanced properties compared with bulk materials, which provides possibilities for new technological applications in various areas. For example, the electronic states for a nanometer-scale semiconductor become partially or completely discrete as in atoms and molecules and the widening of band gap also appears, which enables a higher concentration of carriers to contribute to the band-edge light emission and leads to a reduced emission threshold, improved temperature stability, and a narrower emission line[Klimov 2000-314].

Many methods for preparing nanomaterials have been developed, ranging from electron-beam lithographic techniques to various chemical and physical methods. However, electron-beam lithography is not suitable for large-scale device fabrication and the other methods are always far from the desired control of the final morphology of the produced nanostructures. Thus, a method termed “template synthesis” entails the preparation of a variety of nanomaterials with a desired morphology and provides a path for enhancing nanomaterial order. If the templates have cylindrical pores of uniform diameter in nanoscale, mono-disperse of the desired material can be obtained within the pores of the template material. Anodic aluminum oxide (AAO) prepared by the electrochemical anodization of aluminum with nanoporous structure just become a most potential candidate as the role. As shown schematically in Figure 1-1[Asoh 2001-B152], the nanoporous structure is consisted of self-organized vertical pore channel array with

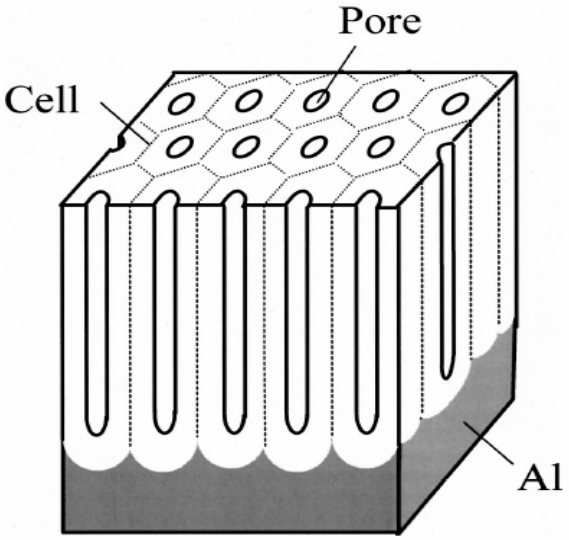

Figure 1-1 Schematic drawing of the idealized structure of AAO[Asoh 2001-B152].

hexagonal arrangement and tunable pore diameters of ten to several hundred nanometers depending on the anodization conditions employed[Li 1998-6023]. Owing to such charming features, the AAO templates have been widely used to construct highly ordered, purposefully designed, and massively parallel nanotubes[Li 1999-367; Liu 2002-1391], nanofibres[Hsieh 2004-1186], nanowires[Ding 2004-2361; Li 2000-2011; Liu 2003-838], nanorods[Mei 2005-021111; Stoleru 2004-5152], and nanodots[Liang 2004-5974; Masuda 2000-1031] of metals, semiconductors, carbons, polymers, and other solid materials. The nanopores filled with desired material by electrochemical[Sauer 2002-3243; Wang 2001-3847] and electroless[Nishizawa 1997-1923] depositions, sol-gel deposition[Lakshmi 1997-2544], hydrolysis process[Lei 2001-1125; Zhang 2001-2511], physical vapor deposition (PVD)[Liang 2002-2544], and chemical vapor deposition (CVD)[Zhang 2001-5714; Liu 2003-838; Lee 2001-2387] are major template synthetic approaches. By using the AAO templated synthesis, the nanostructured materials are produced at a potentially low cost, which can serve as promising candidates for electronic[Davydov 1999-3983; Kouklin 2002-1649], optoelectronic[Liu 2003-838; Ding 2004-2361], and magnetic[Lee 2002-8513] nanodevices as well as reinforcement nanocomposites.

1.2 Motivation

Carbon nanotubes (CNTs) are quasi one-dimensional (1-D) nanostructures of carbon bonded by sp^2 and sp^3 bonds with hollow and cylindrical construction. One can simply image that CNT is a graphene sheet shaped like a roll in nanometer scale, as shown in Figure 1-2. Due to many unique properties, such as high aspect ratio, small

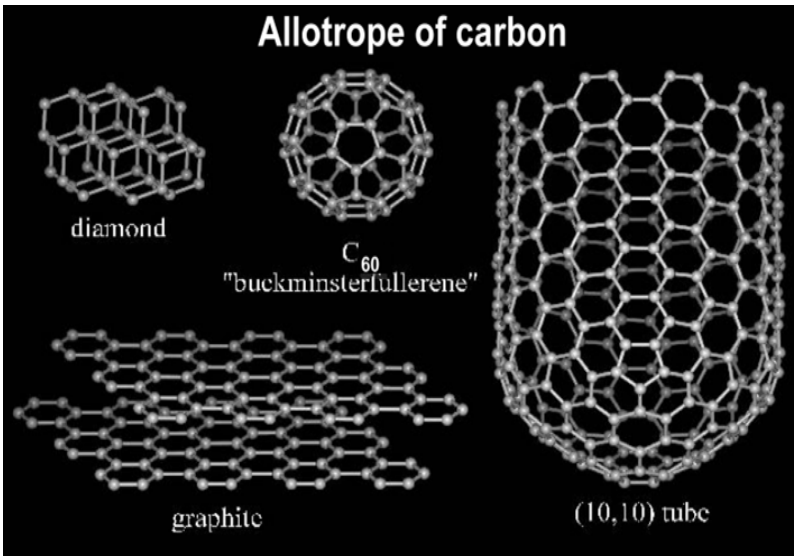

Figure 1-2 The allotropes of carbon: graphite, diamond, C_{60}, and CNTs.

radius of curvature at the tip, extraordinary mechanical strength and chemical stability, etc., undoubtedly, CNTs can be drown on many applications including field emission displays (FEDs), field effect transistors (FETs), hydrogen storage, chemical sensors, etc. For the practical application to FEDs or high performance vacuum microelectronic devices, it is necessary to grow vertically aligned CNT arrays on a large area with suitable packing density and ordered arrangement. As for this requirement, the template methods are widely applied to produce well aligned and mono-dispersed CNT arrays. Ordered arrays of CNTs have been fabricated by using the nanoporous AAO membranes as the template by several research groups[Kyotani 1996-2109; Li 1999-367; Iwasaki 1999-2044; Suh 1999-2047; Yao 2001-11395; Bae 2002-277]. They generally use a high-temperature thermal CVD process for catalyst pyrolysis of hydrocarbon precursors to grow CNTs. CVD enhanced by plasma is another potential alternative to dissociate the precursor gases with more efficiency at low temperature. In this study, we propose the preparation of the AAO templated CNT arrays by microwave plasma electron cyclotron resonance CVD (ECR-CVD). ECR reactors are simple to generate and offer a high ionization efficiency compared with dc or rf capacitive discharges. Highly aligned CNT arrays have been successfully grown in the AAO nanopores by using the ECR-CVD. Field emission measurements confirm that the AAO templated CNT arrays are excellent electron field emitters. Moreover, field emission properties of CNTs are critically affected by a field-screening effect caused by the proximity of neighboring tubes[Nilsson 2000-2071]. It is necessary to well control the length and the tube number density of the tubes. Although

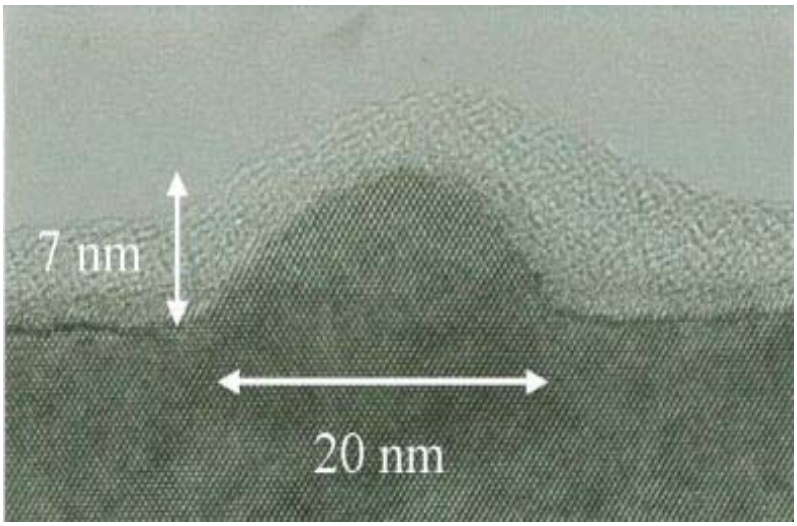

Figure 1-3 HRTEM image of a self-organized InAs quantum dot grown on GaAs substrate.

the length of CNTs can be immediately controlled by changing the growth time, control on the tube number density is still challenging. Here, we propose a simple method to control the tube number density of the CNT arrays on the AAO template directly during the ECR-CVD growth. Enhanced field emission properties of the CNTs are obtained by lowering the tube density.

Quasi zero-dimensional (0-D) nanostructured materials, including nanodots, quantum dots, nanoislands, nanoparticles, etc., are isolated crystals or atomic clusters in nanometer scales. They have also stimulated much attention because of both the scientific importance of understanding the behavior of quantum confinement as well as the technological significance of their promising applications in next generational optical and optoelectronic devices, quantum computing, and information storage, etc. The majority of previous studies have focused on those fabricated by the self-organized Stranski-Kranstanov (S-K) growth in strained heterostructures[Eaglesham 1990-1943]. Figure 1-3 shows a high-resolution transmission electron microscopy (HRTEM) image of a self-organized indium arsenide (InAs) quantum dot grown on gallium arsenide (GaAs) substrate. However, the S-K growth is constrained to a few material systems and size ranges in which the critical strain-mismatch conditions can be met. Moreover, this method always results in random positioning and a broad size distribution in the nanodots[Gilberto 1998-353], causing a wide range of property fluctuations. In this study, we propose a reproducible and inexpensive method by employing the nanoporous AAO films as the template for local anodic oxidation of metal films to fabricate ordered arrays of metal oxide nanodots. Self-organized nanodot arrays of titanium oxides are

formed by electrochemical anodization of an Al/TiN bilayered film. This novel method not only can realize highly ordered nanodot arrays with narrow dot-size distribution, but also overcomes the limitation of the S-K mode growth. We have investigated the phase development of the isolated titanium oxide nanodots, which is very much different from the cases of thin films and powders. Moreover, the field emission properties of the nanodots are characterized and a field emission triode device using the nanodot arrays as emitters is proposed. The nanodot emitters show potential for application in FEDs and vacuum microelectronic devices.