行政院國家科學委員會專題研究計畫　成果報告

奈米結構沉積製程與積體電路製程之整合

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行政院國家科學委員會專題研究計畫成果報告

奈米解析度記錄媒體及其他應用之包覆合金碳奈米結構陣列，其製造、機械/熱性質及製程特徵之研究

子計畫三(3/3)-奈米結構沉積製程與積體電路製程之整合

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中文摘要

本計畫第三年度主要的研究內容為利用陽極氧化鋁(anodic aluminum oxide, AAO)做為模板, 在矽基板上製作奈米碳管(carbon nanotubes, CNT)三極體場發射結構陣列。製作過程首先在矽晶片上直接製備 AAO 模板，並在其通道中利用電子迴旋共振化學氣相沈積系統成長奈米碳管，接著於其上沉積氧化層與電極層，最後由反應離子蝕刻系統完成三極體開口結構。利用掃瞄式電子顯微鏡與拉曼光譜比較蝕刻前後碳管的微觀結構與光譜差異，可證明蝕刻製程對於碳管的破壞很小。在場發射性質方面，此結構擁有約 8.05 伏特/微米的啟始電場。

關鍵詞：碳奈米管、陽極氧化鋁、場發射

Abstract

Carbon nanotubes (CNT) were grown in anodic aluminum oxide (AAO) and used as field emitters in a triode structure. To fabricate the field-emission triode structure, nanoporous AAO thin layer was first prepared on the Si (100) substrate, followed by the growth of vertically aligned carbon nanotubes in AAO pore channels by electron cyclotron resonance chemical vapor deposition (ECR-CVD). The SiO_2 dielectric and Al gate electrode layers required for the triode structure were directly deposited on the CNTs. Reactive ion and wet etches were then used to open the field-emission area in the triode. Scanning electron microscopy and Raman spectroscopy studies revealed that damage to CNT emitters in the etched area was trivial. Field-emission characteristics of the CNT emitters have been studied and a turn-on field of ~ 8.05 V/μm was measured.

Keywords
carbon nanotubes (CNT), anodic aluminum oxide (AAO), field-emission

1. Introduction

Carbon nanotubes (CNT) have many desirable properties as a source of field electron emitters, such as high aspect ratio, small radius of curvature, high mechanical strength and chemical stability.[1-3] Therefore, carbon nanotubes have attracted wide interest in the development of field-emission flat panel displays (FED) using CNTs as field emitters. For FED applications, it is necessary to grow vertically aligned CNT arrays on a large area with suitable tube density and tube diameters. In many CNT-FED studies, CNT emitters on the cathode panel are prepared either by direct catalytic chemical vapor deposition or screen-printing.[4-7] Field screen effect often degrades field-emission properties of CNT emitters grown by CVD method because the density of CNTs is usually too high to avoid field penetration among adjacent emitters.[8] On the other hand, screen printing method has difficulties to make uniform and well-aligned CNT emitters on the substrate. In our previous study, we have successfully grown vertically aligned and uniform CNTs in the porous anodic aluminum oxide (AAO) template, which was prepared on the Si(100) substrate, by electron cyclotron resonance chemical vapor deposition (ECR-CVD).[9,10] Both the density and length of CNT emitters can be well controlled by tunning the CVD deposition conditions, such as the composition of the gas precursor and the growth time. In this year, we fabricated field-emission triode arrays with the AAO templated carbon nanotubes as the field emitters by standard integrated circuit processes. The field-emission property of the CNT emitters in the triode structure was also studied.

2. Experimental

An Al film 2 μm thick was first evaporation-deposited on the *p*-type Si(100) wafer, and the AAO pore channel array was subsequently prepared by electrochemical anodization in oxalic acid solution. In order to obtain well-aligned pore channels, the AAO fabrication was carried out with the two-step anodization method. This resulted in highly uniform and periodic nanoporous channels in the AAO layer, which were then used as the template for the growth of carbon nanotubes. Cobalt was used as the catalyst for CNT growth, and was electrochemically deposited at the AAO pore bottom in the mixture electrolyte of $CoSO_4$ and H_3BO_3. The CNT growth was carried out at 600^oC in an ECR-CVD system using a gas mixture of 20% CH_4 and 80% H_2 as the plasma source. The carbon nanotubes grown in the AAO template as described above will be abbreviated as AAO-CNT thereafter in the text.

To fabricate AAO-CNT field-emission triodes, standard integrated circuit processes were used. Figure 1 shows the fabrication scheme of the triode array. After the preparation of the AAO-CNT emitters, tetraethoxysilane (TEOS) oxide was deposited on the AAO-CNT layer as the dielectric layer of the triode by plasma enhanced CVD (PE-CVD), and followed by the evaporation-deposition of an Al layer as the gate electrode. The Al top layer and the oxide dielectric were etched by a high density plasma reactive ion etching (HDP-RIE) system. After the RIE process, buffered oxide etchant (BOE) was used to remove the remnant SiO_2.

3. Results and Discussion

The nanoporous AAO film exhibited highly ordered pore arrangement with a uniform pore size of 70 nm - 80 nm and a pore-to-pore separation about 100 nm. This allows the Co catalyst to be uniformly deposited at the bottom of each vertical pore channel by electro-deposition and acted as catalysts to grow CNTs. Using AAO as the template, the CNTs grew along the axis of pore channels and had a tube diameter compliant with the pore size of the AAO pore channels, resulting in the growth of uniform well-aligned CNTs. In our previous studies, the length and tube density of CNTs extending out of the AAO pore channels could be properly controlled by the growth time and the gas ratio of CH_4 and H_2 in the ECR-CVD system, respectively.[9, 10] Figure 2(a) shows the side-view micrograph of the nanoporous AAO template. The length of most CNTs extending out of the AAO pore surface was ~ 400 nm. Co catalyst particles were found to locate on the tip of the carbon nanotubes, indicating CNT growth in AAO nanopore channels was via the tip growth mode.

To fabricate AAO-CNT field-emission triodes, the dielectric layer and the gate electrode layer were deposited on the uniform and highly aligned CNT emitters on the AAO template. All CNTs were embedded in the SiO_2 dielectric layer of 1.5 μm in thickness as shown in the cross-sectional SEM micrograph of Fig. 2(b**)**. The surface roughness of the SiO_2 dielectric layer was strongly influenced by the length of CNTs extending out of AAO channels and the thickness of the SiO_2 layer. Therefore an appropriate combination of the length of CNTs and the thickness of the dielectric layer is crucial to photolithographically define the pattern of the field-emission triode array. After photolithography, the Al gate layer was reactive-ion etched. The silicon dioxide dielectric layer was then partially removed by RIE using a 50/50% mixture of CHF_3 and Ar (with a gas flow of 80 sccm) as the gas source at a pressure of 10 mTorr. After the RIE process, the remnant SiO_2 was completely removed by BOE wet etch for 5 seconds. Figure 3 shows the SEM image of the AAO-CNT triode array fabricated as described. The triode structure is 6.5 μm in diameter and 2 μm in depth. Uniform and aligned CNTs were well distributed on the the AAO template in the triode structure.

It is generally believed that ion sputtering can alter the microstructure of carbon nanotubes and thus alter the field-emission property. Carbon nanotubes would suffer from ion bombardment as the CNTs in the triode structure were exposed to the plasma during the etch of the SiO_2 dielectric. During the reactive-ion-etch of the SiO_2 dielectric layer, a mixture of CHF_3 and Ar was used, and thus carbon nanotubes were subject to bombardment of various ions, including hydrogen, fluorine, argon and fluorocarbon ions. It has been reported that hydrogen ion bombardment could increase C-H bondings in carbon nanotubes and resulted in a more disordered microstructure.[11] On the other hand, fluorination occurs on the carbon nanotubes when CNTs are treated by fluorocarbon plasma, such as CF_4.[12, 13] In this study, we found that the RIE process to remove partial SiO_2 dielectric layer seemed not to cause obvious damage. Figure 4 shows the SEM image of the AAO-CNT emitters after the dielectric layer was removed by RIE etch for 270 s, followed by BOE etch for 5 s. It can be clearly seen that Co catalyst particles were still present at tips of the carbon nanotubes, implying that the RIE etch induced little damage to the AAO-CNTs. Difference in the length and density of carbon nanotubes between the as-prepared AAO-CNTs and that after the removal of the dielectric layer was hardly perceivable. Figure 5 shows Raman spectra of the as-grown carbon nanotubes on the AAO template and that after the removal of SiO_2 by RIE and BOE etches. The two prominent Raman peaks are located at ~1325 cm^{-1} (D band) and ~1598 cm^{-1} (G band). The former is due to the ring stretching mode in a disordered graphitic structure and the later sp^2 bond stretching mode.[14, 15] Peak features of both Raman modes, such as peak position and intensity, are commonly used to study the insight of the crystallinity and graphitic bonding of carbon nanotubes. The ratio of the integral intensities of the G and D bands, I_G/I_D, can be used to estimate the microstructure disorder of carbon nanotubes. The SiO_2 encapsulated sample had an I_G/I_D ratio about 0.46 after the RIE and BOE etches, and this value was close to that of the as-prepared AAO-CNTs, ~ 0.5. In addition, the two Raman peaks of the etched sample had no apparent peak shift as compared to the counterparts of the as-prepared AAO-CNTs, suggesting that removal of the SiO_2 dielectric layer by RIE and BOE etches did not cause significant chemical and microstructure damage to the carbon nanotubes.

Field-emission measurement of the AAO-CNT triode array was conducted under a vacuum condition of ~ 10^{-6} Torr with a simple diode measurement configuration. A cylindrical probe was placed 100 μm above the AAO-CNT emitters without any electrical connection to the Al gate electrode. The measured field emission current density (J) as a function of the electric field (E) was plotted in Fig. 6. The turn-on electric field (E_{to}), which is defined as the electric field required to produce an emission current density of 1 mA/cm^2, was ~ 8.05 V/μm. The measured E_{to} was higher than those of AAO-CNT emitters grown on a blanket AAO template in our previous work since the triode array had only 1/3 emitting area than the blanket AAO-CNTs.[16] We are setting up a field-emission measurement system, which allows us to apply bias voltage on the Al gate electrode, so that field-emission characteristics of the individual AAO-CNT triodes can be studied.

4. Conclusions

We have successfully fabricated field-emission triodes with carbon nanotubes as the field-emitters. The nanoporous AAO film was used to template the growth of vertically aligned and density tunable CNT emitters in an ECR-CVD system. Standard IC process techniques were used to fabricate the triode structure on the as-prepared AAO-CNT layer. Reactive ion etch and BOE etch, which were carried out to etch away the Al gate electrode and the SiO_2 dielectric layer in the triode structure, made little damage to the AAO-CNT emitters according to SEM and Raman spectroscopy studies. A turn-on electric field of 8.05 V/μm was obtained for the AAO-CNT emitters in the triode array.

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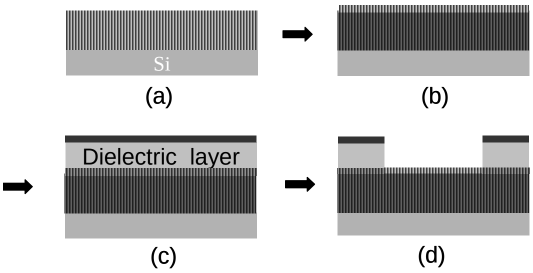

Figure 1. The fabrication scheme of the AAO-CNT triode structure: (a) preparation of the AAO layer on the Si wafer, (b) CNT growth by ECR-CVD deposition, (c) dielectric and gate electrode depositions on the CNTs, and (d) RIE and BOE etches to open the field emission area of the triode.

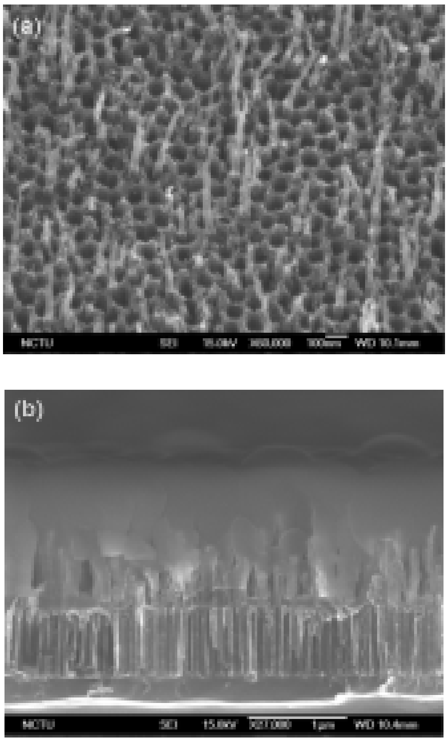

Figure 2. (a) SEM image of the carbon nanotubes grown on the AAO template. (b) Cross-sectional SEM image of the AAO-CNTs capped by the TEOS SiO_2 dielectric and Al gate electrode layers.

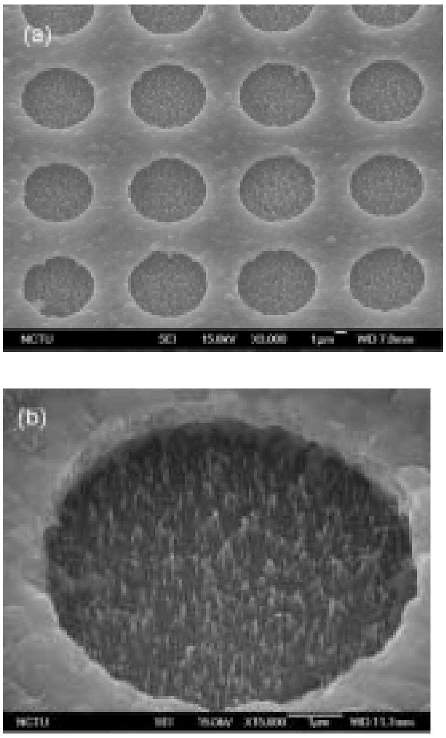

Figure 3. (a) The SEM image of the AAO-CNT triode array. (b) An enlarged SEM image of a single triode.

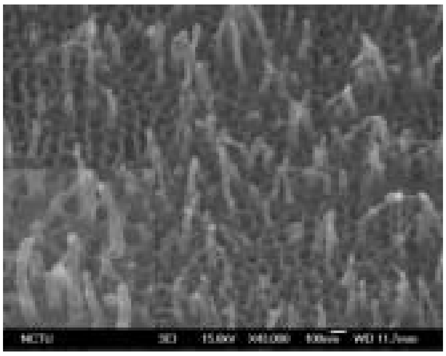

Figure 4. SEM image of the AAO-CNTs after RIE etch for 270s and BOE etch for 5s. The inset is an enlarged image of the carbon nanotubes.

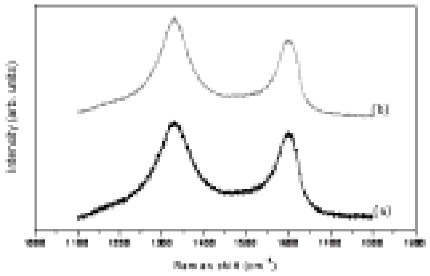

Figure 5. Raman spectra of (a) the as-prepared AAO-CNT emitters and (b) the SiO$_2$ capped AAO-CNTs after RIE etch for 270s and BOE etch for 5s.

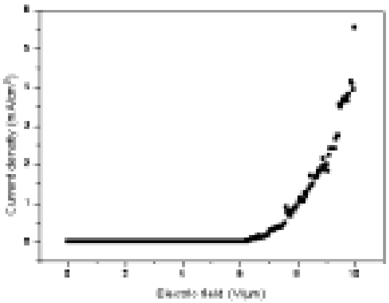

Figure 6. Field emission current density (J) - electric field (E) characterization of the AAO-CNT triode array.