第 25 卷第 11 期 半 导 体 学 报 Vol. 25, No. 11
2004 年 11 月 CHINESE JOURNAL OF SEMICONDUCTORS Nov., 2004

Influence of Pretreatment Conditions of Stainless Steel Substrates on Field Emission Properties of Carbon Nanotubes Films

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Abstract: Carbon nanotubes (CNTs) are synthesized from methane and hydrogen gas mixture directly on stainless steel plates by microwave plasma chemical vapor deposition (MWPCVD). By varying pretreatment conditions of the substrates such as mechanically polishing and acid washing, it is found the polishing and acid washing can lower the turn-on field and improve the emission current density. The current density of the un-pretreated sample attains 1.2mA/cm^2, but the polished sample and polished acidly washed sample attain 3.2 and 2.75mA/cm^2, respectively, at the electric field of 6.25V/μm.

Key words: carbon nanotube; MWPCVD; field emission; Raman spectroscopy
PACC: 7970; 8120V; 6116D
CLC number: O462.4 **Document code**: A **Article ID**: 0253-4177(2004)11-1349-06

1 Introduction

Carbon nanotubes (CNTs) have attracted much attention because of their unique structure and properties since their discovery[1]. One important potential application for CNTs is as electron field emission sources in flat panel displays and electron guns[2~7]. The high aspect ratios and small tip radius of curvature together with high chemical stability and high mechanical strength of the CNTs are outstanding advantages for electron field emission. Two basic types of methods are presently available to prepare CNTs field emission cathode. The first one is screen printing method by using CNTs paste[4,6]. The large screen cathode can be made, but it is difficult to control the uniform distribution of CNTs. The CVD method is the second one that is ideally suited to grow film of nanotubes on pre-coating substrates with a metallic catalyst layer, which has been reported by many authors[8~11]. In this paper, we reported the CNTs films synthesized directly on stainless steel substrates by MWPCVD without pre-coating of catalyst layer, and especially investigated the influence of pretreatment conditions of substrates on field emission from such deposited carbon nanotubes films.

2 Experiment

Stainless steel plates were used to be substrates as the combined catalyst and supporting material for the synthesis of CNTs, the diameter of stainless steel plates is 6mm. The CNTs were prepared in a microwave plasma chemical vapor deposition (MWPCVD) system. The source gas for

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Received 24 February 2004, revised manuscript received 29 April 2004

growing the CNTs was a mixture of H_2 and CH_4, the hydrogen gas serves as both etching reagent for the formation of catalyst nanoparticles issued from the substrate and diluted gas. The typical gas flow rates of H_2 and CH_4 were 100 and 8sccm, respectively, with total pressure of 6.5×10^3Pa. Substrate temperature was maintained at 700℃. The deposition time was kept for 10min. Three various examples of A, B, and C were prepared, which correspond to different pretreatment conditions of substrates. The substrate of sample A was a un-pretreated stainless steel plates; the substrate of sample B was mechanically polished by various SiC polishing powders (the diameters are 20, 10, and 5μm respectively); the substrate of sample C was mechanically polished and then acidly washed to further etch the surface, following a rinse with distilled water, then cleaned in an ultrasonic bath with acetone and methanol for all of them.

Scanning electron microscopy (SEM) was used to determine the morphology of carbon nanotubes. Raman spectroscopy was used to analyze the structure of carbon nanotubes directly on the stainless steel substrates. A Renishaw system 2000 micro-Raman spectrometer was utilized at excitation wavelength of 632.8nm. The line shift was calibrated by comparing the spectra with that of silicon. Using a 50μm slit, the spectral resolution was better than $1cm^{-1}$. Laser intensity on the sample was about 3mW. The field emission characteristics of the samples were measured by using a diode structure. The transparent anode was made of an ITO coated glass plate. The CNT samples as the cathode were separated from the anode by a mica sheet with a suitable hole as the emission area. The gap between the anode and the cathode was 120μm. The measurement was conducted under pressure of 3.6×10^{-5}Pa.

3 Results and discussion

Figure 1(a) shows the typical current versus electric voltage for CNT emitters of samples A, B, and C. The bias voltage sweeps were conducted several times and Figure 1(a) shows the forth sweep. After the fourth measurement, the current is well stabilized. A relatively large amount of current at higher voltage in each sweep probably caus-

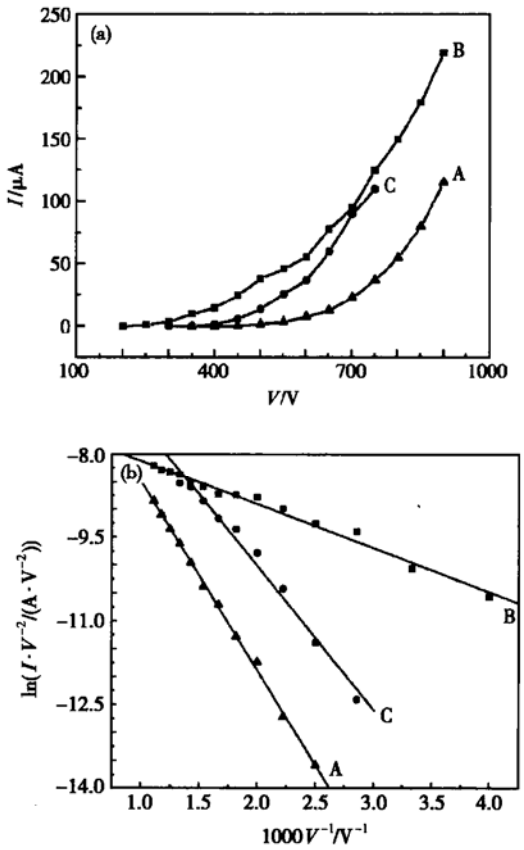

Fig. 1 (a) Current versus voltage (I-V) curves; (b) Fowler-Nordheim (F-N) plots obtained from the samples A, B, C

es some annealing[12], and after a few sweeps, the structure of the nanotubes seem to reach a stable configuration. CNTs on untreated steel begin to emit electrons at a higher electric field level than CNTs on pretreated steel substrates, indicating that the emission property of CNTs depends on the pretreated condition of substrate. The turn-on applied electric fields (corresponding to the current density of $10\mu A/cm^2$) of samples A, B, and C are 2.92, 1.67, and 2.5V/μm, respectively, and emission current density of samples A, B, and C reaches value of 1.2, 3.2, and $2.75mA/cm^2$ at electric field of 6.25V/μm, respectively. Figure 1(b) shows the

corresponding Fowler-Nordheim (F-N) plots [ln (I/V^2) versus $1/V$]. The F-N plots of the three samples almost follow a linear relationship over the measuring range, which indicates that the electron emission from these samples complies with a conventional tunneling mechanism, described by Fowler-Nordheim theory. The slope S of the F-N plot is $S = -B\Phi^{3/2}d/\beta$, where d is the interelectrode distance, $B = 6.83\times10^9 eV^{-3/2}\cdot m^{-1}$, Φ is the work function, and β is the field enhancement factor defined as $E_l = \beta E$, where E_l is local electric field, E is macroscopic field between two electrodes. Determining the value of the slope from F-N plot and assuming $\Phi = 4.7eV$ for CNTs, as for graphite, it is possible to derive the field enhancement factor β. The field enhancement factors β of samples A, B, and C are 2467, 10583, 3249, respectively. According to the F-N equation $I \propto (E_l^2/\Phi)\exp(-B\Phi^{3/2}/E_l)$, it is reasonable to conclude that the emission properties of sample B with lower turn-on electric field and largest emission current density are related to the largest field enhancement factor β. The polishing pretreatment of substrate probably leads to β increasing. Therefore, it is necessary to do polishing pretreatment for substrate for the successful synthesis of CNTs in MWPCVD system.

TEM was employed to characterize the structure of three samples. To prepare TEM samples, the samples were transferred to a carbon coated copper grid. The specimens for TEM were first peeled off by a pair of tweezers from the stainless steel plate and dispersed in alcohol by ultrasonic treatment, then dropped onto holey grids. The typical TEM image of three samples is shown in Fig. 2. TEM images show that the as-formed products contained abundance of nanotubes. Most of the nanotubes are bent and a multi-walled structure.

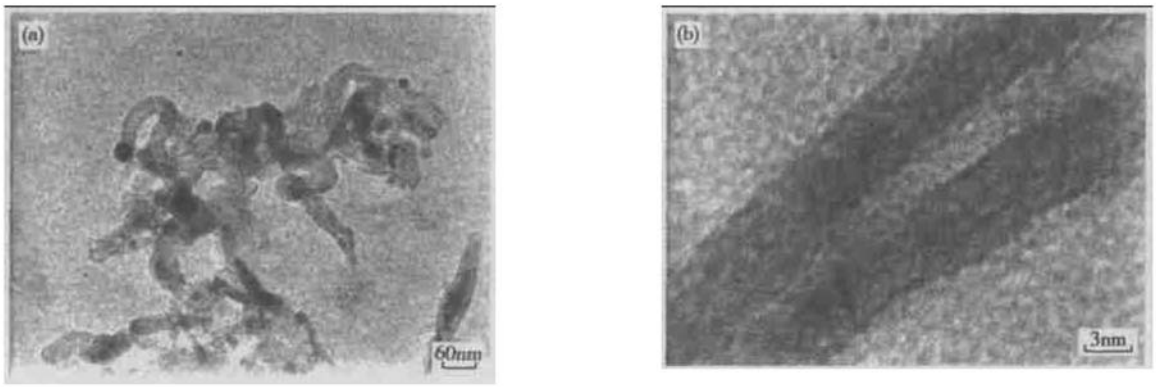

Fig. 2 TEM images of carbon nanotubes films (a) Low magnification TEM image of CNTs; (b) High resolution TEM image of a CNT with graphite wall layers and a hollow tube structure

Figure 3 shows the SEM picture of stainless steel in conditions A and B. It is seen that the polishing roughens the surface and produces many irregular protrusions (shown in Fig. 3(b)), the size of which is about several micrometers.

Figure 4 shows the SEM pictures of CNTs films. It can be seen that there are CNTs with high density grown in conditions A, B, C. It means that hydrogen plasma should transform a part of Fe and Ni in the stainless steel substrate into catalyst nanoparticles for the growth of CNTs before CH_4 was introduced in the case of metallic substrates, in contrast to metallic catalyst thin films coated substrates, which transform into particles or islands. But mechanisms for the formation of nano-sized catalyst particles are not well understood.

Figure 4(b) shows the surface morphology of the CNTs films in the case of condition B. It is obviously seen that the CNTs of sample B are uniform with the highest density and lest quantity amorphous carbon. In contrast, in conditions A and C, the CNTs do not show the uniform (shown in

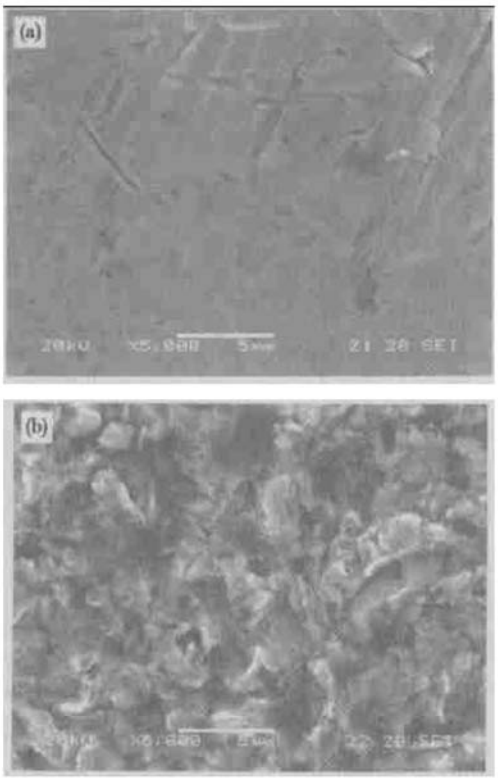

Fig. 3 SEM pictures of stainless steel in conditions A and B (a) Un-polished; (b) Polished

Figs. 4(a) and (c)), and especially there are more metal clusters in condition C, which is probably due to a increasing active of the catalyst particles with the decrease of its size. The gathered metal clusters as catalyst lose active for formation of CNTs and cause the electric field screening effect on those adjacent carbon nanotubes, which is subject to lower field enhancement factors than that of sample B.

In condition B, the possible reason for the high field enhancement factor (β= 10583) is suggested. In experimental situation B, the polishing pretreatment of substrates were carried out by micro powders, so that irregular protrusions were formed (shown in Fig. 3(b)) on the surface of the substrates, which would cause a field enhancement factor β_1 on the top of the protrusions, and the CNTs deposited on the protrusions produce another field enhancement factor β_2, therefore the overall enhancement factor $\beta = \beta_1\beta_2$ leads to a high field enhancement.

Figure 5 gives the Raman spectra of CNTs

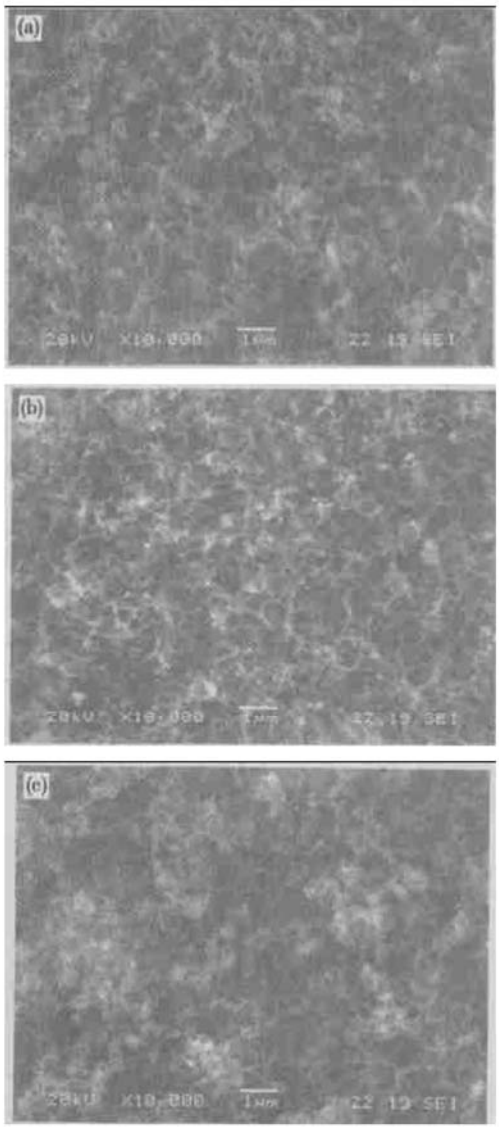

Fig. 4 SEM images of carbon nanotube films (a) Sample A; (b) Sample B; (c) Sample C

films grown in conditions A, B and C. The D peak (disordered line) has been known to be due to the carbonaceous particles, defects in the curved graphieic sheet, tube ends, and finite size of crystalline domains of the tubes[13]. The strength of the D-line relative to the G-line (I_D/I_G) is a measure of the amount of disorder in the nanotube material. The G-line peak arising from zone-center E_{2g} mode of highly oriented pyrolytic graphitic (HOPG) is located at 1582cm^{-1}. The G-line peak position for the CNTs films exists a blue shift, which probably comes from catalytic particles inside nanotubes[14]. The deviation of G-line relative to 1582cm^{-1} and

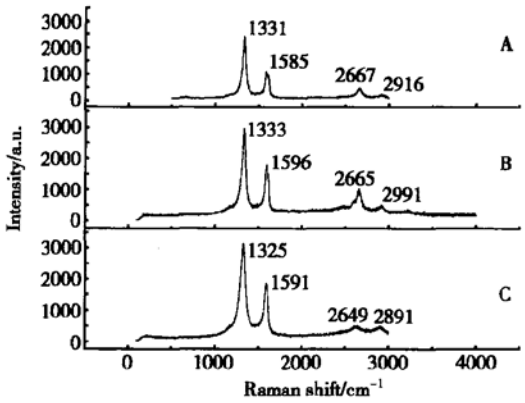

Fig. 5 Raman spectra corresponding to samples A, B, C

corresponding I_D/I_G are listed in Table 1. The shift of G-line of sample B is the largest one among the three samples, which means more catalyst particles in nanotube walls for sample B, so that an increased defect density occurred in sample B. Probably, this is another reason leading to large emission current density in sample B.

Table 1 I_D/I_G and shift of G-line (relative to 1582cm^{-1}) of samples A, B, and C

Sample	A	B	C
I_D/I_G	2.1826	1.6371	1.6766
Shift of G-line/cm^{-1}	3	14	9

4 Conclusion

In summary, CNTs film on stainless steel plates by MWPCVD without pre-coating of catalyst are fabricated. It is found the various pretreated condition of substrates influence the field emission characteristics of CNTs film. The mechanically polishing and acid washing can lower the turn-on voltage and improve the emission current. The polished sample shows the best field emission properties.

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不锈钢衬底的预处理条件对碳纳米管薄膜场发射性能的影响

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摘要: 在不同预处理条件的不锈钢衬底上, 利用微波等离子体化学气相沉积(MWPCVD)方法从甲烷和氢气的混合气体中沉积碳纳米管薄膜, 并对其场发射性能进行了研究. 实验发现, 不锈钢衬底的机械抛光和酸洗, 能降低碳纳米管膜的开启场强, 增大它的发射电流密度. 在场强为 6.25V/μm 时, 衬底未处理样品的电流密度为 1.2mA/cm^2, 而衬底抛光的样品和衬底抛光又酸洗的样品的电流密度分别达到 3.2 和 2.75mA/cm^2. 衬底只需机械抛光, 而不需要酸洗, 就能改良碳纳米管膜的场发射性能.

关键词: 碳纳米管膜; MWPCVD; 场发射; Raman 光谱

PACC: 7970; 8120V; 6116D

中图分类号: O462.4 **文献标识码**: A **文章编号**: 0253-4177(2004)11-1349-06

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2004-02-24 收到, 2004-04-29 定稿