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Adhesive enhancement improved field emission characteristics of carbon nanotube arrays on energetic ion pre-bombarded Si substrates

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Abstract: Field emission (FE) characteristics of well-aligned multiwall carbon nanotube arrays (CNTAs) grown on originally polished and energetic iron ion bombarded Si substrates were investigated. It was found that the FE characteristics have been improved remarkably by the pretreatment of iron ion bombardment, an evident promotion of the highest emission current density from 4.05 mA/cm^2 to 54.45 mA/cm^2 was as an expression of this enhancement, this enhancement in characteristics is attributed to the improved adhesion between CNTs and Si substrate for the existence of iron buffer layer. The relationship between adhesive force and emission current density has been introduced, and the calculation reveals that the adhesion has been enhanced by 14.4 times due to the energetic ion pre-bombardment on Si substrate.

Introduction

Since the discovery of carbon nanotubes (CNTs) by S. Iijima in 1991 [1], numerous works have been done for the improvements in the growth process [2-4] and the investigation of various properties, which may be utilized in different applications, such as cold electron sources in electron microscopes [5], x-ray tubes [6] and flat panel display (FPD) emitters [7] based on carbon nanotube arrays (CNTAs). At present, screen-printing [8] and thermal chemical vapor deposition (TCVD) [9] are two main methods employed to fabricate FPD emitters based on CNTs. Low-cost and being easy to large-scale fabrication features are advantages shown in screen-printing method, while CNTAs synthesized by TCVD method, for their eminent FE characteristics exhibited in stability and high emission current density, has also aroused extensive interests for its potential application. For FE behaviors of CNTs, great efforts have been paid, hitherto, such as ameliorate adhesion between substrates and CNTAs by the introduction of buffer layer [10], high temperature annealing [11], low work function elements doping [12,13] and so on.

In the present paper, FE characteristics of well aligned CNTAs grown on original and ion pre-bombarded Si substrates have been investigated, and the relationship between adhesive force and emission current density have been discussed.

Experimental Details

In order to understand the influence of iron buffer layer on FE characteristics, two substrates (n (100)-Si) were prepared, one was the originally polished Si substrate without any treatment and the other was exposed to iron ion beam at 10 keV for 15 minutes to form a buffer layer. Then, 5 nm-thick iron film was deposited on both of the substrates by direct-current magnetron sputtering as the catalysts for CNTs growth. CNTs were synthesized by TCVD at 750 ℃ in a tubular furnace. Prior to the growth of CNTs, ammonia gas with a flow of 200 standard cubic centimeters per minute (sccm) was utilized as etching gas to improve the activity of catalyst. During CNTs growth, a mixture of hydrogen and acetylene with a flow rate of 6.9:1 was used as carrying gas and reactive gas, respectively, the growth time was 30 minutes and all these processes were carried out in ambient pressure.

The morphology of CNTAs was examined by field emission scanning electron microscopy (SEM) (JSM-4800), and Raman spectroscopy has been employed to examine the crystallization of CNTs. For FE measurements, a diode configuration with a moveable anode which was placed in a vacuum chamber with a basic pressure of 1.0×10^{-7} Pa was employed, and CNTAs stuck to a copper plate were the cathode. The distance between the tip of CNTAs and the anode was kept at 2.362 mm during our measurements, and the areas of all the samples used in this experiment were about 0.04 cm^2, all the tests were carried out at room temperature. The experimental data is automatically recorded by a computer connected to the measurement system.

Results and Discussions

SEM was utilized to examine the morphology of CNTAs synthesized on different substrates. Fig.1 shows the side-view images of CNTAs, a) c) and b) d) are corresponding with CNTAs grown

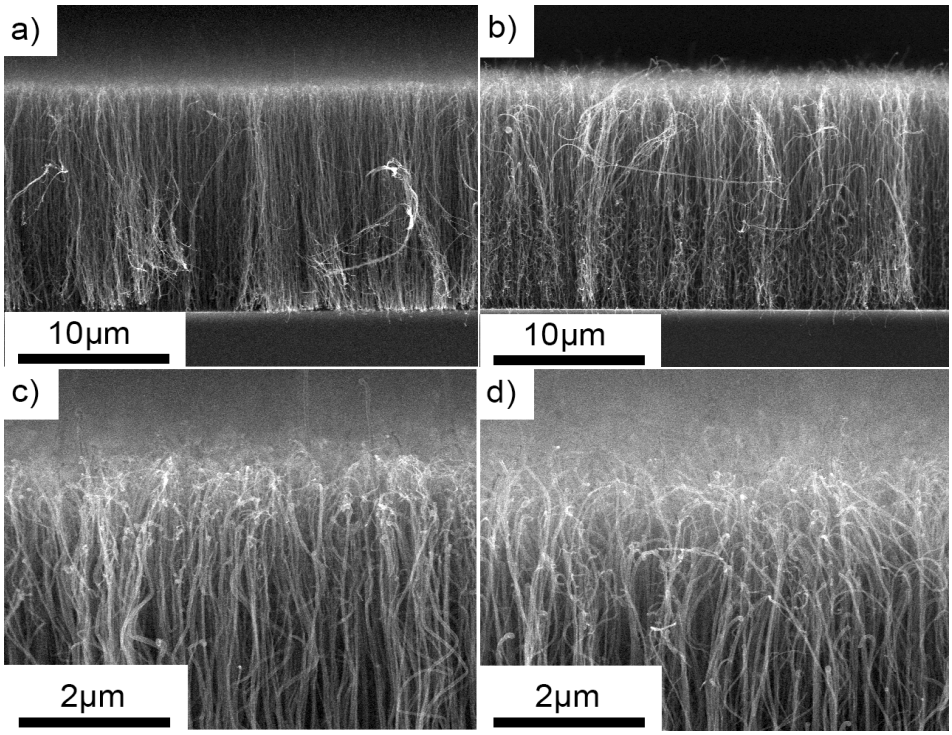


Fig. 1 SEM side-view images of CNTAs synthesized on different substrates. a) and b) are low-resolution SEM images which show a panoramic view of the CNTAs, c) and d) are amplified SEM images of the near-top of CNTAs. a), c) and b), d) are corresponding with CNTAs grown on original and iron ion pre-bombarded Si substrates, respectively.

on original and iron ion pre-bombarded Si substrates, respectively. It can be found that both of the nano-arrays are about 20 μm in length. The differences in the panoramic view of CNTAs, as shown in Fig.1 (a) and (b), are obvious. The vertical alignment morphology in CNTAs grown on original Si substrate is better than those grown on iron ion pre-bombarded Si substrate. While CNTAs synthesized on iron ion pre-bombarded Si substrate have a curved and thinly packed morphology in the bottom half. This difference in the density of CNTs can also be seen in the amplified SEM images, as shown in Fig.1 (c) and (d), the density of CNTs grown on original Si substrate is larger than the other one. Another difference which can be seen from these images is that the mean diameter of CNTs synthesized on original Si substrate is smaller than that of the other. All of the differences can be attributed to that part of the pre-bombarded iron blends in the 5 nm-thick catalyzed iron, and both of them play as the catalyst in the growth of CNTs, this incorporation of catalyst can, in a certain degree, increase the diameter and reduce the density of the catalyzed grains which determine the diameter and density of CNTs.

Fig. 2 shows the curves of emission current density versus applied fields (J-E curves) and Fowler–Nordheim (F-N) plots of the CNTAs grown on different substrates. The turn-on electric fields (E_{on}, the applied field when emission current density is 10 μ A/cm^2) of the CNTAs grown on polished and ion pre-bombarded Si substrates are 1.050 V/μm and 1.081 V/μm, respectively.

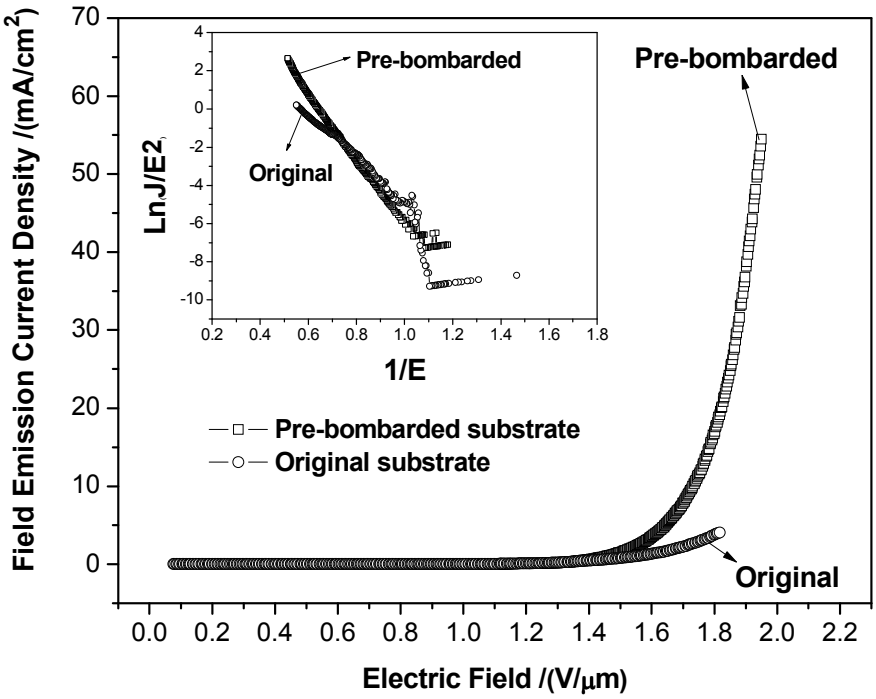
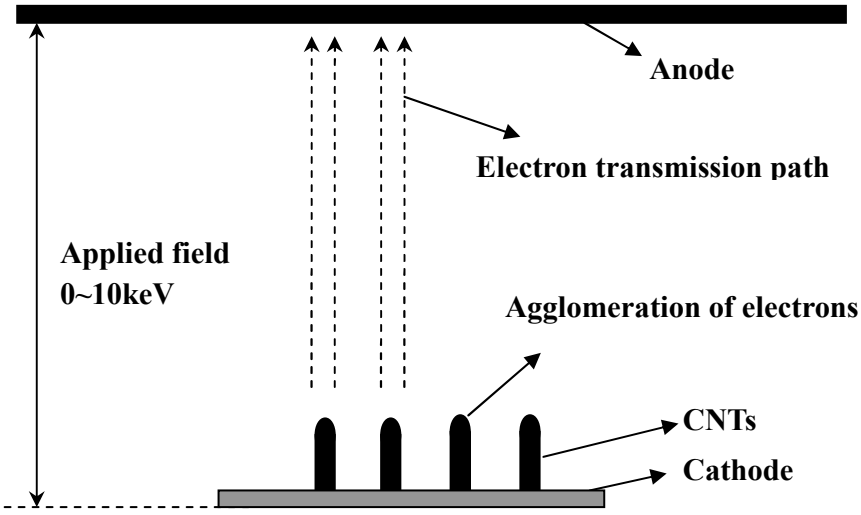


Fig. 2 J-E curves of CNTs grown on originally polished and energetic ion pre-bombarded Si substrates, the inset is the corresponding F-N plots.

The difference in E_{on} is not so obvious, because during field electron emission, part of CNTs, especially those extrude from others (larger aspect ratio), will undertake a larger local electric field at the tip for the less influence of field-screening effect [14], so they will contribute more emission current than others during field emission, which means that the E_{on} is mainly determined by those extruded CNTs. In this study, all the samples were synthesized in the same condition, although differences can be observed, as shown in Fig. 1, the structural differences in the tip of CNTAs, in the statistical point of view, are small, so the difference in E_{on} is negligible.

The highest emission current density (HECD) of CNTAs grown on polished and ion

pre-bombarded Si substrates, which is obtained when a breakdown occurred in the electron filed emission process, is 4.05 mA/cm^2 and 54.45 mA/cm^2, respectively, which means that a more than 10 times enhancement have been introduced to HECD by the process of iron ion pre-bombardment



on the Si substrates. This improvement can be attributed to the enhanced adhesion between CNTs Fig. 3 Schematic illustration of the field electron emission process and the generation of electrostatic force between the agglomerated electrons at the tip of CNTs and the positive charges in the anode.

and Si substrates for the existence of iron buffer layer, because during field electron emission, CNTs will undertake a large force, which can take them off from the substrate [15]. This force exists in the form of electrostatic force and induced by the electrostatic interactions between electrons which agglomerate in the tip of CNTs and the applied field of the anode plate. The field electron emission process has been schematically illustrated in Fig. 3. It's not hard to imagine that the applied field between anode and cathode will lead an agglomeration of electrons in the tip of CNTs and positive charges at the surface of the anode plate, and electrons will emit from the tip of CNTs when the electrostatic force is larger than the bonding force, and, obviously, the emission current density (J) is relative to the agglomerated electron density (ρ) at the tip of emitters during field electron emission. We conceive that J is proportional to ρ, and then a simple approximate equation can be given as:

$$J = K\rho \tag{1}$$

where K is a constant, and ρ is the charge density agglomerated at the tip of CNTs. Another approximation is that the electric field between the tip of CNT and anode is uniform (ideally), i.e., E = constant, the electrostatic force of electrons per unit area (F) can be expressed as:

$$F = \rho E \tag{2}$$

By combining Eq. 1 and Eq. 2, the relationship between electrostatic force and emission current density can be expressed as:

$$F = JE/K \quad (3)$$

Therefore, the electrostatic force ratio of CNTs synthesized on different substrates can be given by:

$$F_{pre\text{-}bombarded} : F_{original} = J_{pre\text{-}bombarded} : J_{original} \quad (4)$$

Taking the experimental results into Eq. 4, $F_{pre\text{-}bombarded} : F_{original}$ is about 14.4, which means that the critical force for the breakdown occurring in the FE process has been greatly promoted for the introduction of iron buffer layer, and this improved adhesion between CNTs and the Si substrates can greatly enhance the field emission properties of CNTs, especially the HECD.

Conclusions

FE characteristics of CNTs grown on originally polished and energetic iron ion bombarded Si substrates have been investigated. The highest emission current density for CNT arrays grown on the originally polished and energetic ion pre-bombarded Si substrates is 4.05 mA/cm^2 and 54.45 mA/cm^2, respectively. The diversification in FE properties of CNTAs grown on different substrates, especially the highest emission current density, is attributed to the different adhesion between CNTs and substrates. The relationship between adhesive force and emission current density has been discussed, and a simple approximate calculation reveals that the adhesion has been enhanced about 14.4 times due to the energetic iron ion pre-bombardment on Si substrate.

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