SWNTs growth using nano-catalyst-embedded particles

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Abstract

We presented a systematic investigation on the growth of CNTs including SWNTs on nano-catalyst-embedded particles by PECVD. For CNTs growth , the mixture of C_2H_2 and NH_3 was used. The total pressure and temperature were kept at 3.25 Torr and 650 ℃, respectively. Finally, we measured the field emission property from CNTs grown from nano-catalyst embedded zeolite particles in vacuum chamber ($<10^{-7}$ Torr).

1.Introduction

Carbon nanotubes (CNTs) are interested in nanoelecrtonics [1], gas adsorption [2] and electron emission property. Among them, CNTs are an especially promising candidate for cold cathode field emitters because of their unique electrical properties and the highest aspect ratios [3-5].

Therefore CNTs have been the focus of considerable research. Especially single-walled carbon nanotubes (SWNTs) with very small amounts of amorphous carbon and few defects have become possible with nano-catalytic particles [6]. So numerous investigations have been carried out in the growth SWNTs by various methods. However, the growth of vertically aligned SWNTs by Direct Current Plasma Enhanced Chemical Vapor Deposition (DC PECVD) has not been reported yet. DC PECVD takes advantage of low temperature process, low pinhole density and vertically aligned CNT growth, compared to other growth methods [7].

With such merits, we attempt to grow SWNTs as well as MWNTs using nano-catalytic particles embedded supports. Specially, $AlPO_4$-5 (AFI) as nano-catalytic particles has very small pore (~7Å) by itself. So we used nano-catalytic particles embedded in $AlPO_4$-5. The catalytic materials is iron acetate (II). This method allows easily and economically to prepare catalytic particles for CNTs growth.

In this study, we report of various kinds of CNTs have grown by DC PECVD on $AlPO_4$-5 surface with nano-catalyst embedded particles. We report also the field emission experiments of such CNTs in vacuum chamber ($<10^{-7}$ Torr).

2. Experimental

In our experiment, we used measoporous materials as $AlPO_4$-5 powder. In pre-treatement process, $AlPO_4$-5 powder as measoporous material was dehydrated by heating at 400 ℃ for 12h in a air. Silicon wafer with thermal evaporated thin film of aluminum(1000Å of thickness) as an adhesion layer was used as a substrate. As next process, catalytic solution was mixed 5 x 10^{-4} mol/L of $(C_2H_3O_2)_2Fe$ in DI water by sonication for 20 min. And then it was sonicated adding of $AlPO_4$.-5 in Fe acetate solution for 30 min. At this time, the weight ratio of $(C_2H_3O_2)_2Fe$: $AlPO_4$-5 = 1 : 10 was used for next fabrication. The Al-Si substrate was dipped in Fe acetate solution including $AlPO_4$-5 as catalytic powder. After drying at 50℃ for 30min, directly 100℃ for 30min, we have grown CNTs on $AlPO_4$-5/Al-Si substrate by DC PECVD. The substrate was heated by halogen lamp on Ar gas at 650℃, and for the CNTs growth the gas mixture of C_2H_2 and NH_3 was used. To this time, the total pressure and temperature was kept at 3.25 Torr and 650℃ respectively. CNTs growth time was to maintain for 20 min. We present a systematic investigation on the growth of CNTs including SWNTs on $AlPO_4$-5/Al-Si substrate by DC PECVD. We employed SEM and resonance micro Raman analysis for the morphology, diameter, microstructure and chemical bonding of CNTs. Finally, we measured the field emission property from CNTs grown from nano-catalyst embedded $AlPO_4$-5 in vacuum chamber ($<10^{-7}$ torr).

3. Results and discussion

The SEM micrographs of the $AlPO_4$-5 as mesoporous powder is shown in Fig. 1. Each figure is shown bare $AlPO_4$-5 (a), catalytic mesoporous powder as $AlPO_4$-5 (b) and $AlPO_4$-5 including CNTs (c). Fig. 1(a) and Fig. 2(b) show that the surface of $AlPO_4$-5 is not changed by catalytic composition. Also Fig. 2(c) shows that $AlPO_4$-5 is not transformed by plasma effect during CNTs growth by DC PECVD.

Figure 2 shows that $AlPO_4$-5 grains located separately on the surface of Al-Si substrate, i.e. $AlPO_4$-5 particle is not to conglomerate each other. Also, there are many of CNTs have grown on Al surface of substrate. The main feature of CNTs on $AlPO_4$-5 surface is smaller diameter than on Al surface.

One can see from Fig . 2(b) and Fig. 2(c) the different diameters of CNTs. CNTs on the surface of Al-Si substrate have an average 50 nm of diameter, on other side, CNTs on $AlPO_4$-5 have smaller diameter about 20 nm. In these case, $AlPO_4$-5 has catalytic smaller volume than the surface of Al-Si substrate. Catalytic volume is largely controlled by the geometry of the pore of $AlPO_4$-5

To identify CNTs growth at different sections of Al-Si substrate Raman spectroscopy were accurate measured. It is well known that Raman spectroscopy is widely used for research of CNTs properties. The excitation wavelength was performed 514.5 nm to study the detailed configuration of CNTs [7]. According to M.L. Chapelle [8] and M.S. Dresselhaus [7], the radial breathing mode (RBM) of frequency of SWNTs located between 130 and 260 cm^{-1}, G band of frequency located between 1500 and 1600 cm^{-1}. Otherwise the D band and G band of frequency of MWNTs located respectively about 1330 and 1590 cm^{-1}

Fig. 3 presents various sections of $AlPO_4$-5, Al-Si surface. Figure 3(a), 3(b), 3(c) and 3(d) demonstrate different patterns by optical microscope (x 800). Raman spectrum exhibits ambiguously the characteristic frequencies of CNTs [7]. The peaks centered at 138 cm^{-1}, 1338 cm^{-1} and 1596 cm^{-1} show to be of wide distribution various kinds of CNTs on $AlPO_4$-5/Al-Si substrate.

Finally, we carried out the field emission property from CNTs growth on surface of $AlPO_4$-5 /Al-Si substrate. Figure 4 shows the field emission characteristics of CNTs on $AlPO_4$-5 /Al-Si substrate. Spacing between anode and CNTs on $AlPO_4$-5 /Al-Si substrate was 242 μm. To measure field emission properties a parallel diode-type configuration was used in vaccum chamber with vaccum pressure at 5 x 10^{-7} Torr. The measurement for electron-emission density was estimated from the open-window area of aluminum oxide spacer (0.5 cm x 0.5 cm). As shown in Fig. 4, according to the Fowler-Nordheim (FN) plot, the emission current can be expressed by $I \propto (E^2_l/\o)$ x $\exp(-B\o^{3/2}/E_l)$, where $B=6.83 \times 10^9 (VeV^{-3/2}m^{-1})$ and $\o$ is the work function. We assumed the work function of the nanotube to be 5.0 eV [9]. The local electric field (E_l), can be related to the field enhancement (β) and macroscopic field (E_m) by $E_l = \beta E_m$. The field enhancement factor can be calculated from slope of the FN plot. The slope S of the FN plot is equal to $S=-B\o^{3/2} d/\beta$, where d is the inter-electrode distance (the thickness of a spacer). The value calculated β is equal to 720.

The turn-on field is defined as the electric field where the emission cuttent occurs in FN plot and turn-on electric field (E_{to}) voltage was defined as the electic field at 10 μA /cm^2 of the current density. As shown in Fig. 2, the E_{to} was 4.0 V/ μm.

4. Conclusion

In this paper, we demonstrated the possibility of CNTs growth in mesoporous powder as $AlPO_4$-5 with embedded nano-catalyst particles. This method should be useful to get CNTs. This also could be useful for producing FED based on highly dispersed mesoporous materials.

The analysis of Raman spectra has shown the present of different kinds of CNTs including SWNTs. The first testing experiments were performed which are shown the reasonable parameters of FED and potential applications of CNTs on mesoporous powder.

5. References

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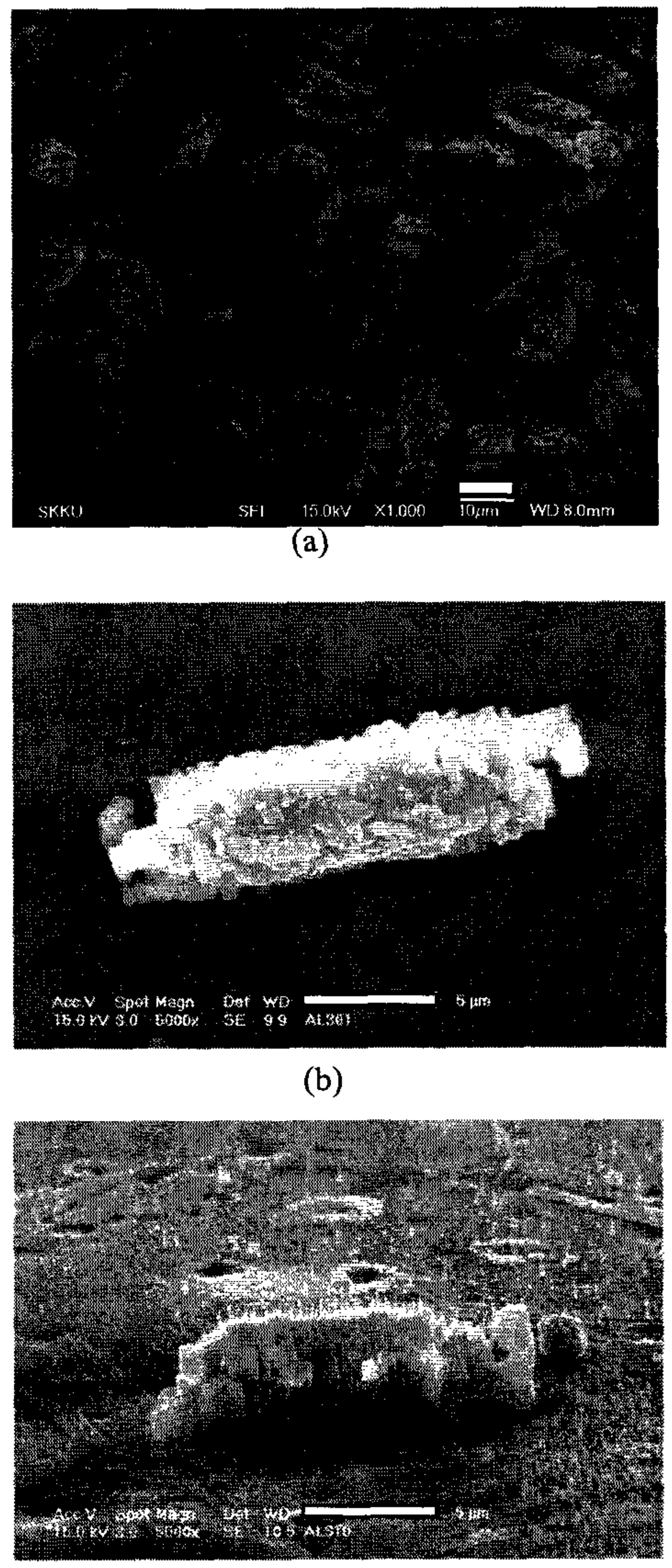
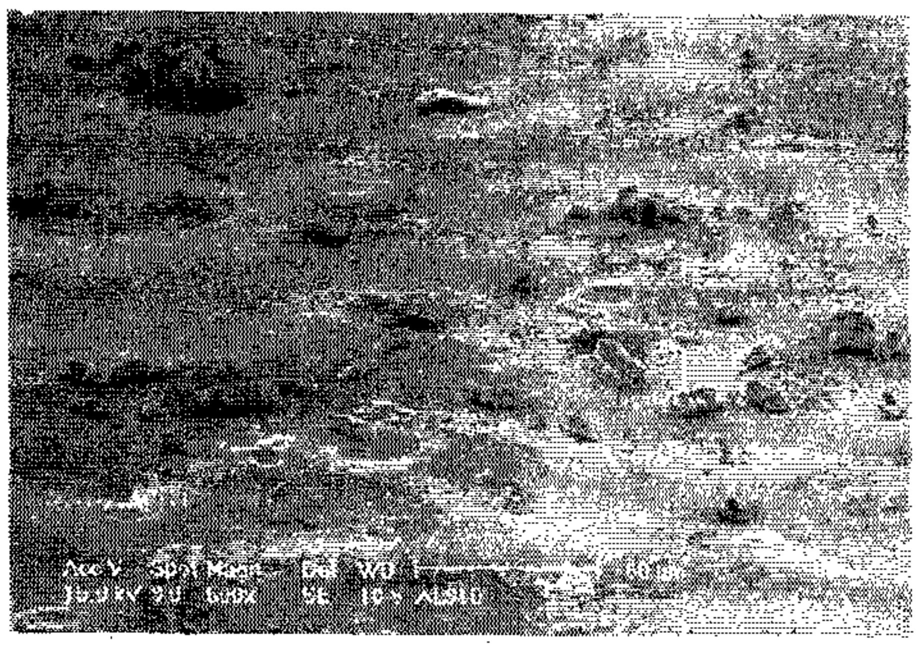
6. Figures

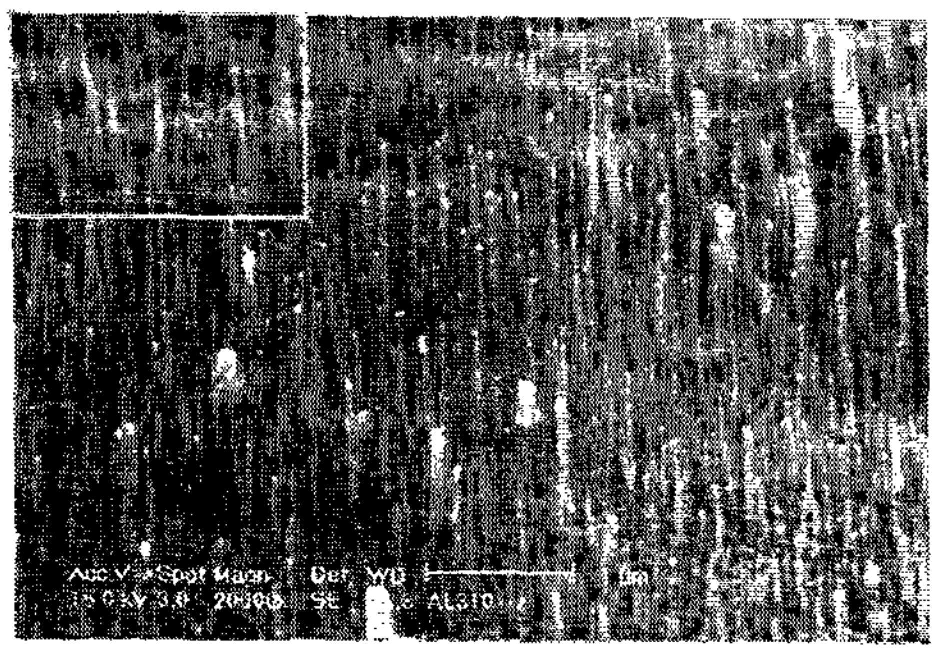


(a) (b) (c)

Fig 1. SEM image of (a) bare $AlPO_4$-5 (b) catalytic particle as $AlPO_4$-5 (c) $AlPO_4$-5 including CNTs



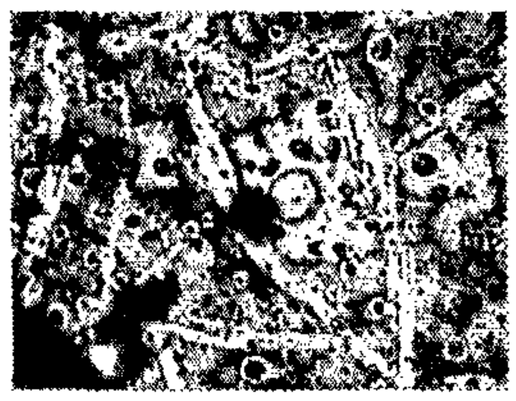
(a)



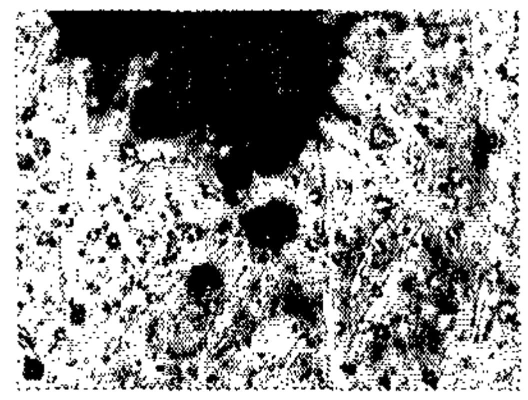
(b)

(c)

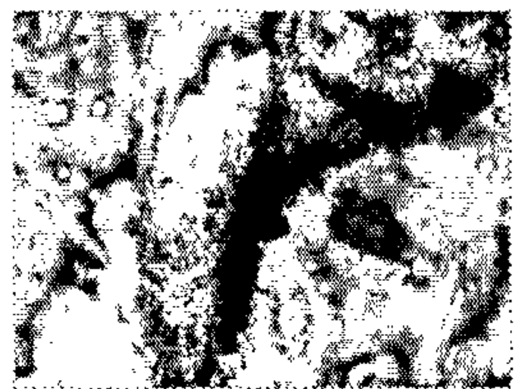
Fig 2. SEM image of (a) CNTs growth on surface of $AlPO_4$-5 /Al-Si substrate (b) surface of Al-Si surface (C) CNTs growth on $AlPO_4$-5



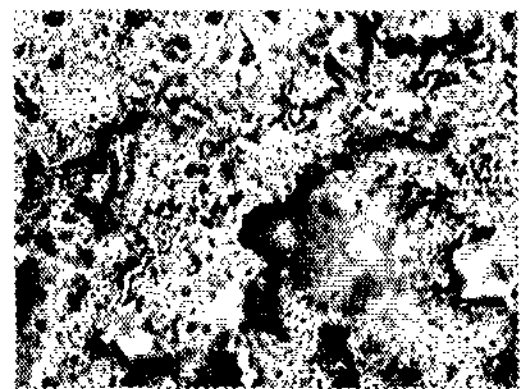
(a)



(b)



(c)



(d)

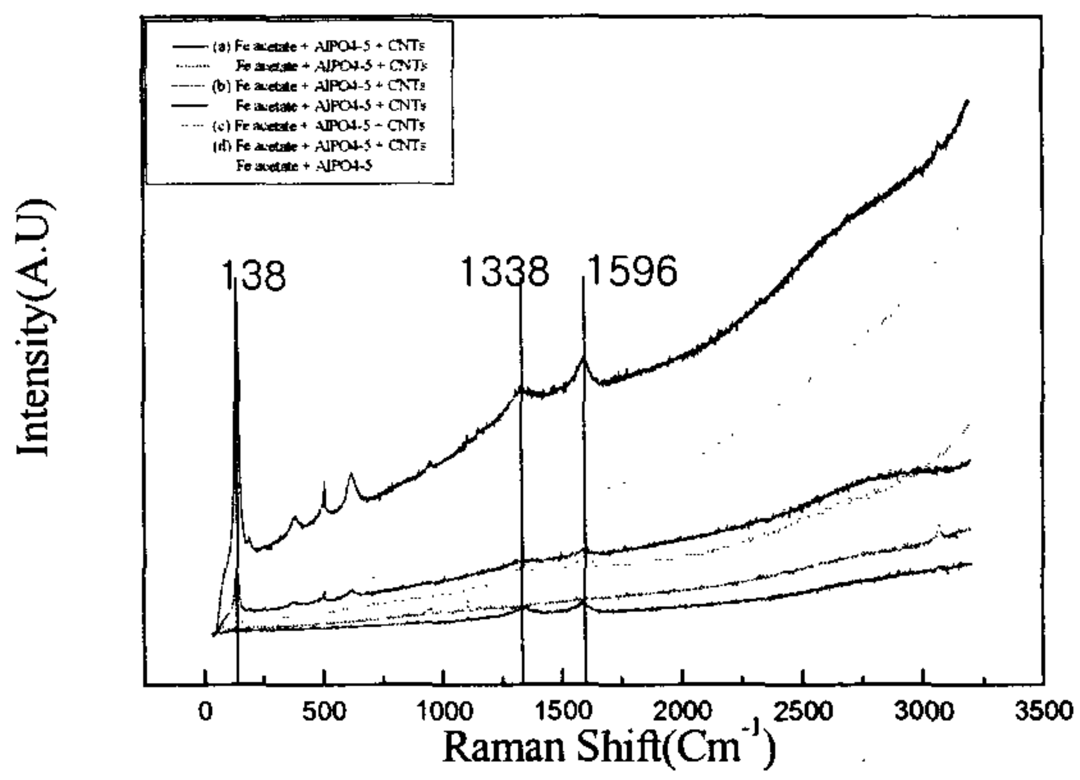


Fig 3. Optical microscope and Raman spectroscopy. (a),(b),(c),(d) are different sections of $AlPO_4$-5 /Al-Si substrate.

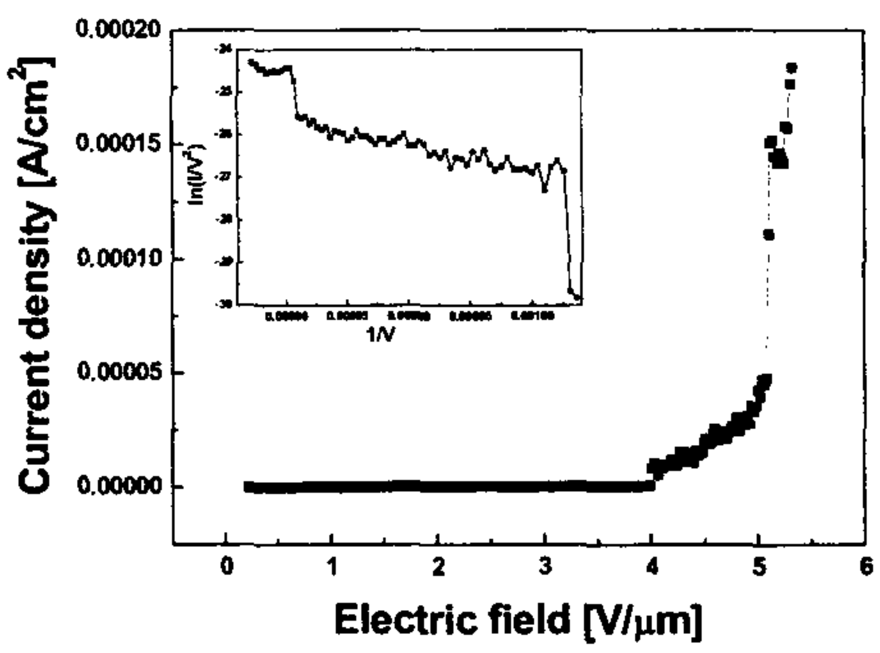


Fig 4. *Field emission characteristics of CNTs on $AlPO_4$-5 /Al-Si substrate.* A Fowler-Nordheim plot of emission current and field emission current density