Constructing Ag nanoparticles–single wall carbon hybrid nanostructure to improve field emission properties

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ABSTRACT

The overall process of field emission can be dominated by the contact resistance between the single wall carbon nanotubes (SWCNTs) and the substrate. In order to reduce the contact resistance, we present a wet chemical process of constructing Ag–SWCNTs hybrid nanostructure. Constructing Ag–SWCNTs emitters could improve the electrical contact by increasing the contact area between SWCNTs and substrate. Contact resistance is greatly reduced compared to that of pristine SWCNTs. Field emission properties of Ag–SWCNTs hybrid emitters including current density and emitting image are remarkably improved. Field emission properties based on the modified Fowler–Nordheim (F–N) equation are discussed. Our studies show that this method can enhance the field emission properties of the SWCNTs by improving the contact resistance and is a promising way for mass production of SWCNTs for field emission display.

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1. Introduction

Since single wall carbon nanotubes (SWCNTs) possess high aspect ratio, distinguished mechanical, chemical, electrical and physical properties, they have been vastly studied by several research groups [1–4]. Many electronic devices such as field emission displays have been fabricated in recent years [5]. The field emission properties of the carbon nanotube (CNTs) based devices have been widely investigated [6–9] and the characteristics of the CNTs field emission were always interpreted within the framework of the classical Fowler–Nordheim (F–N) law [10]. But for practical CNTs based field emission devices, the contact resistance between the substrate and emitters may be another issues in nanoelectronics. In general, the reported electrical contact resistances between the CNTs and the substrates are very large [11–14], and such high resistance greatly prevents CNTs based devices from reaching the intrinsic electronic properties of CNTs. The field emission current of CNTs deposited on substrates will be greatly tailored by this contact effect [15,16]. The presence of resistances in series can induce the current saturation at high applied electric fields or a large voltage drop along the CNTs emitter and at the CNTs/substrate interface [17–19]. The resistance in series with the contact and emitters may

be a key factor in limiting the field emission of CNTs because the electrons emitted from CNTs depend on the efficiency of the electron injection from substrate into one-dimensional nano-structural emitters. As field emission electron sources, CNTs must have low resistance to the electrode so that they can exhibit excellent field emission performance.

Based on the above reasons, for improving the contact resistance, this article presents a wet chemical process of decorating Ag nanoparticles on SWCNTs surface to increase the contact area between SWCNTs and substrate. The contact resistance between SWCNTs and the Si substrate had been greatly reduced in the room temperature. The field emission properties of the SWCNTs field emitters made using this method was significantly improved compared to that of pristine SWCNTs. We expect that the constructing Ag–SWCNTs hybrid nanocomposite in this article will be an easy way to fabricate SWCNTs based field emission cold cathode.

2. Experimental processes details

2.1. Materials preparation

The raw SWCNTs used in this study were synthesized by the chemical vapor deposition (CVD) method and the SWCNTs were typically 1–2 nm in outer diameter and 5–30 μm in average length. The raw SWCNTs were pretreated by ultrasonic agitation in solution with 1:3 volume ratio of concentrated nitric and sulfuric

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acid for 24 h. And then they were washed with deionized water and dried in air at 120 °C for a long time. Owing to acid treatment, carboxylic acid groups are introduced to the defect sites of the SWCNTs. Pretreated SWCNTs (1–3 mg) were added into 50 ml analytically pure isopropyl alcohol that contained dissolved $Mg(NO_3)_2 \cdot 6H_2O$ at a concentration of 1×10^{-4} M. This dispersion was first sonicated with a high power horn for 1 h. A little quantity of SWCNTs dispersion was diluted in 200 ml isopropyl alcohol and than followed by sonication for about 5 h in a bath sonicator.

2.2. Electrophoretic deposition SWCNTs and Ag nanoparticles decorating

The first step was the electrophoretic deposition (EDP) of SWC-NTs on n-type Si substrate [20]. A piece of silicon wafer (cathode) and a stainless-steel plate (an anode) were immersed into the SWCNTs electrophoresis suspension at room temperature. The two electrodes were kept in parallel with a gap of 1 cm held constant by two glass spacers. The deposition was carried out by applying a constant DC voltage of 40 V and the deposition time was kept at 10 min. Soon after finishing the deposition and dried in the atmosphere condition, the SWCNTs covered on the Si wafer were put into dilute nitric acid solution in order to remove $Mg(OH)_2$ or MgO covered on SWCNTs surfaces. The second step was the synthesis of SWCNTs/Ag nanohybrid material. In this process, dimethyl sulfoxide (DMSO) has been used as reducing agent and trisodium citrate dehydrate as capping agent to control the size of the nanoparticles. 1 g of $AgNO_3$ was added to 50 ml of DMSO and stirred at 60 °C using a magnetic stirrer followed by the addition of 1.5 g of trisodium citrate. The Si substrate covered on with SWCNTs film was putted into the $AgNO_3$ mixtured solution for about 1 h. When picked up from the $AgNO_3$ mixtured solution and the SWCNTs film covered on Si substrate were slowly washed many times with deionized water. The samples were annealed in ambient N_2 at 200–400 °C for 1 h to induce strong adhesion with the substrate.

2.3. Characterization

The morphology of the SWCNTs-supported Ag nanoparticles was characterized and analyzed by scanning electron microscopy (SEM) transmission electron microscope (TEM). The Raman spectra were measured with a laser Raman spectrophotometer. The excitation wavelength of the Ar ion laser was 514.5 nm. The phase structures of Ag nanoparticles were performed by X-ray diffractometer (XRD). X-ray photoelectron spectroscopy (XPS) spectrum was done by VG ESCALAB MARK II spectrometer using Mg Kα (1253.6 eV) as X-ray source. The resistance of SWCNTs film was measured by four-point probe method and contact resistances were measured using the four-wire method. The field emission characteristics were measured with the diode structure in a vacuum chamber maintained at a pressure of 1×10^{-5} Pa at room temperature. The SWCNTs emitters and a phosphor-coated indium-tin oxide (ITO) glass were used as the cathode and the anode, respectively. Direct voltage was applied to the anode, and the emission current was also measured at the anode.

3. Results and discussion

The raw SWCNTs in our studies are mixed with impurities such as amorphous carbon (a-C), so the content of a-C in the raw SWC-NTs should be estimated. Fig. 1 shows the Raman spectra of the raw SWCNTs. It was obtained at the room temperature with the laser wavelength of 514.5 nm, shows the characteristic breath and tangential band at 169–270 cm^{-1} (inset of Fig. 1) and 1592 cm^{-1}, respectively, while the characteristic peak of amorphous carbon is at 1349 cm^{-1}. The content of a-C can be calculated by the following
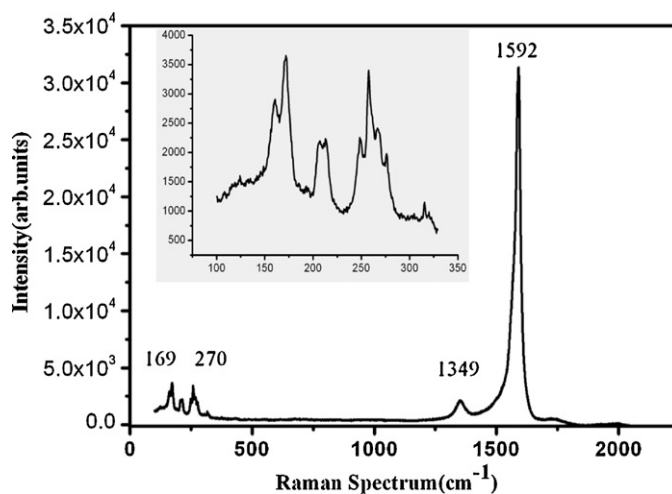

**Fig. 1.** Raman spectrum of the raw SWCNTs.

formula [21]

$$\left(\frac{I_D}{I_G}\right)_{\text{Raw SWCNT}_S}$$

$$= M_{\text{a-C}} \times \left(\frac{I_D}{I_G}\right)_{\text{a-C}} + M_{\text{Pure SWCNT}_S} \times \left(\frac{I_D}{I_G}\right)_{\text{Pure SWCNT}_S} \quad (1)$$

In formula (1), M means the molar ratio of the a-C and the SWCNTs in the raw product, $M_{\text{a-C}} + M_{\text{pureSWCNTs}} = 1$.

The I_D/I_G value for raw SWCNTs is 0.70, which can be calculated in Raman spectrum as shown in Fig. 1. From many studies, the pure SWCNTs have very small I_D/I_G value [21–24]. Here, when it is assumed to be 0.01 for pure SWCNTs. The value of I_D/I_G for a-C is similar to that of MWCNTs [21,25,26], so the calculated concentration ratio between amorphous carbon and SWCNT is about 5.26%. It is obvious that the raw SWCNTs are highly pure with little amorphous carbon.

Fig. 2(a) shows the SEM image of the SWCNTs film before decorating. The SWCNTs present a well-distributed shape with uniform bundle size on Si substrate. In the right side of Fig. 2(a) is TEM image of the SWCNTs before Ag nanoparticle decorating. Fig. 2(b) shows the SEM image of SWCNTs/Ag nanocomposites. The Ag nanoparticles are attached in a highly dispersed state on the surface of SWCNTs, and the average particle size is estimated to be around 60 nm in diameter. In the right side of Fig. 2(b) is TEM image of SWCNTs film with Ag nanoparticles hybrid nanostructure.

Fig. 3(a) gives the XRD pattern of SWCNTs/Ag hybrid material. The peaks centered at 26° and 43° correspond to (0 0 2) and (1 0 0) reflections of the graphitic planes of the SWCNTs, respectively. The peaks assigned to (1 1 1) and (2 2 0) are the planes of the cubic phases of Ag in its face centered crystal structure. The peaks centered at 33° and 69° correspond to (2 0 0) and (4 0 0) reflections of the phases of Si. The reduction of $AgNO_3$ by DMSO proceeds according to the following total reaction, which is proposed to proceed via the initial complex formation of $(CH_3)SO$: to metal species [27].

$$2Ag^+ + (CH_3)SO : + H_2O \rightarrow 2Ag^0 + (CH_3)SO_2 + 2H^+ \quad (2)$$
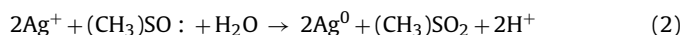
In order to further investigate the interfacial interaction, XPS analysis was used to study the chemical state of the Ag-nanoparticle. As shown in Fig. 3(b), the binding energies at 368.3 and 374.3 eV correspond to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, respectively. The binding energies of Ag 3d in Ag/SWCNTs are slightly difference in literatures, which may be caused by the nature of the dispersion state, the support materials, the particle size, and so on [28–30]. The atomic sensitivity factors of Ag and C are 0.205 and 2.25, respectively [31]. According to XPS spectrums, the quantification results