Diamond & Related Materials 18 (2009) 307–311

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Growth of vertically aligned carbon nanotubes on glass substrate at 450 °C through the thermal chemical vapor deposition method

Tsung-Yen Tsai [a], Nyan-Hwa Tai [a,*], K.C. Chen [b], S.H. Lee [b], L.H. Chan [b], Y.Y. Chang [b]

[a] Department of Materials Science and Engineering, National Tsing-Hua University, Hsin-Chu 30013, Taiwan
[b] Display Technology Center (DTC), Industrial Technology Research Institute (ITRI), Hsin-Chu 30013, Taiwan

ARTICLE INFO

Available online 7 September 2008

Keywords:
Carbon nanotubes
Low temperature CVD
Glass substrate
Co/Ti binary catalyst

ABSTRACT

This work demonstrates the growth of vertically aligned carbon nanotubes (CNTs) on glass substrate at a low temperature of 450 °C. The Co/Ti films prepared by the sputtering method were adopted for growing CNTs in a rapid heating and cooling chemical vapor deposition (CVD) chamber. It was found that the presence of Ti layer played an important role for catalyzing the CNT growth, and CNTs can not grow on glass substrate without Ti layer. CNTs can be synthesized at 450 °C on glass substrates by using the bimetallic film with Ti fractions of 38 and 48%; on the other hand, no CNT can be obtained when Ti with a fraction of 77% was adopted. The results obtained in this work were compared with the predictions based on the Ti–Co binary phase diagram. Besides glass substrate, for comparison, this study also deposited the same bimetallic catalyst on Si substrate and performed the growing process at 500, 600, and 700 °C. According to the results obtained in this study, a two-step processing to prevent the catalyst from poisoning during CNT synthesis is proposed.

1. Introduction

Carbon nanotubes (CNTs) are considered to be a promising cold cathode material due to their high aspect ratio, superior chemical, electronic, and mechanical properties [1–3]. On the fabrication of field emission device, glass is the best substrate, which has the strain point at about 550 °C [4–6]. Two primary methods were adopted for fabricating CNT field emitters on glass substrate, one is the conventional screen printing method which adopts CNT paste containing CNTs, conducting powder, and binder, as the raw materials, and the other is direct growth of CNTs on the glass substrate at low temperature [7–11]. In the screen printing method, CNTs were usually synthesized by arc-discharge, laser ablation [12–14], or chemical vapor deposition (CVD). There are at least two drawbacks in the screen printing method: (i) the entangled CNT bundles can not be dispersed easily during the mixing process, and (ii) CNTs are unable to protrude from the paste after screen printing, which cause non-uniform CNT distribution and poor electron emission property [15]. Therefore, in order to improve the electron emission properties of the screen-printed CNT films, surface treatments such as adhesion taping, soft rubber rolling, ion irradiation, plasma exposure, laser treating, etc. have been used [16–20]. In addition to the screen printing method, thermal plasma and hot filament CVD were employed to grow CNTs directly on the glass substrates [21–26]. Thermal CVD has become an important technique in the fabrication of CNT emitters, because it enables vertically aligned CNTs grown on a large substrate without or with catalyst pattern pre-coated using the lithography technique. However, there still exists a critical problem that is how to reduce the high processing temperature for preventing substrate damage. Many researchers have made efforts to grow CNTs on Si substrate at a lower temperature of 500 °C by using the Co/Ti binary catalysts [27–29]. They preheated the precursor gas at 700 °C in front zone of the furnace to decrease the growth temperature in rear zone; during the process, some other researchers pretreated the catalyst at 1000 °C. In this work, we demonstrate a convenience method to grow CNTs on glass or Si substrates at a temperature between 450 and 550 °C using the Co/Ti bimetallic catalyst. Based on our knowledge, 450 °C is the lowest temperature used in thermal CVD for growing vertical CNTs on glass substrate [28]. It has been found that the binary catalyst has higher activity than that of the pure Co at relatively low temperature and both Ti fraction and substrate influence the CNT growth. The height of synthesized CNTs and its morphologies were also examined.

2. Experimental

The catalysts were prepared in the forms of layered type and hybrid type, which were formed using the co-sputtering and the general sputtering methods, respectively. In the hybrid catalyst, Ti and Co were sputtered at the same time, and the designed composition of the catalyst was controlled by adjusting the DC power source. In the layered catalyst, Ti and Co layers (0.2–10 nm) were sputtered in sequence on glass (Corning, 1737F) and Si substrates by using the multi-target DC power sputter deposition system. Before sputtering, the glass and the Si substrates were pre-cleaned in ultrasonic acetone for 10 min, and then were dried with nitrogen by air gun. After sputtering, the sample was placed in a cold-wall rapid heating and cooling CVD chamber, which was evacuated to 3 mTorr

* Corresponding author. Tel.: +886 3 574 2568; fax: +886 3 573 7406.
E-mail address: nhtai@mx.nthu.edu.tw (N.-H. Tai).

0925-9635/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2008.09.001

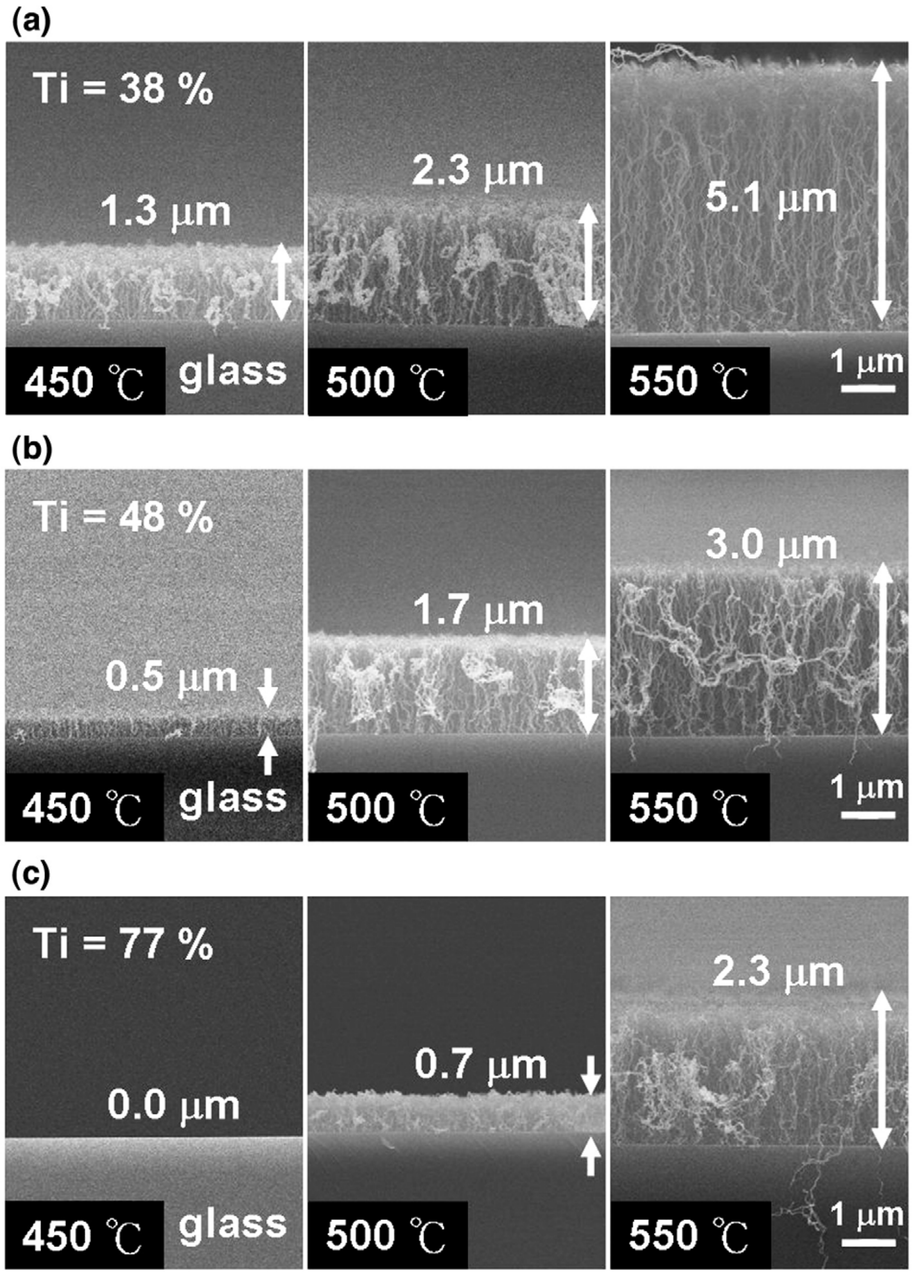

Fig. 1. FESEM images using Co/Ti as catalyst for growing CNTs on glass substrates, (a), (b), and (c) are the cases corresponding to atomic Ti fraction of 38, 48, and 77%, respectively. In each row, the images depicted from left to right are the results obtained at 450, 500, and 550 °C.

before deposition. The mixture of 10% H_2/Ar (30 sccm) gases, acted as the reduction agent and buffer gas, was introduced into the reactor at the pressure of 10 Torr. The sample holder (heater) was then heated from room temperature to the processing temperatures of 450–700 °C within 2 min and was maintained at the desired temperature for 5 min. Subsequently the C_2H_2 gas was channeled into the reactor at a flow rate of 60 sccm to grow CNTs for 5 min. The morphologies and the microstructures of the synthesized CNTs were analyzed by the field emission scanning electron microscope (FESEM, JEOL 6500F) and the high-resolution transmission electron microscope (HR-TEM, JEOL 2010), respectively.

3. Results and discussion

Based on the Ti–Co binary phase diagram [29], three ratios of Co to Ti of catalyst compositions were adopted to investigate the effect of Ti fraction on the CNT growth onto the glass substrates. Thicknesses of the Co/Ti composite layers were 0.5/0.5, 0.6/1.0, and 0.2/1.0 (nm/nm), corresponding to Ti atomic fractions of 38, 48, and 77%, respectively. The catalyst-coated samples with different Ti fractions were preceded for growing vertically aligned CNTs at temperatures of 450, 500, and 550 °C. Length of the synthesized CNTs varies significantly with temperature and Ti fraction, as shown in Fig. 1(a), (b), and (c).

According to the Ti–Co binary phase diagram, Ti/Co bimetal with Ti atomic fraction of 77% has the lowest melting point and better dissolving ability for carbon atoms, which provides good environment for CNT growth theoretically. However, based on SEM image shown in Fig. 1(c), CNTs can not be synthesized at 450 °C on glass substrate by using the catalyst with Ti fraction of 77%. On the other hand, the catalysts with Ti fractions of 48% and 38% performed very well. The tendency is consistent with the results reported in Sato's work which revealed that the best composition for Co/Ti catalyst is 80/20 when