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SCIENCE DIRECT
Surface & Coatings Technology 200 (2006) 3215 – 3219
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Synthesis of ultra long vertically aligned carbon nanotubes using the rapid heating and cooling system in the thermal chemical vapor deposition process

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Available online 10 August 2005

Abstract

Vertically aligned carbon nanotubes (CNTs) were synthesized on a lithographically patterned silicon/silica substrate coated with an ultra thin iron film. The process was performed using different thickness of iron700 – 900 °C using a rapid heating and cooling system (RHCS) in a thermal chemical vapor deposition (CVD) chamber. The substrate was placed on the heater, which can be heated from room temperature to 900 °C within 20 s, and cooled from 900 °C to 250 °C within 25 s. Acetylene was used as the carbon precursor and the mixture of hydrogen and argon was adopted as carrier gas. An ultra high growth rate up to 50 μm/min was detected and a vertically aligned thick CNT array near 500 μm was attained under a low reaction pressure of 10 Torr. The control of CNT layer thickness on the silicon and the silica-patterned substrates was studied. Furthermore, the effects of iron layer thickness on the growth rate and the diameter of the vertically aligned CNTs were also investigated.

Keywords: Carbon nanotube; Vertically aligned; RHCS and CVD

1. Introduction

Due to the unique physical, chemical, mechanical, and electronic properties, carbon nanotubes (CNTs) have been studied extensively since the discovery of CNTs in 1991 [1], and many applications have been proposed [2–4]. The growth of well aligned vertical CNT array is a challenging task for most of the researchers. Different methods aiming at this goal have been proposed [5–18]. Among the articles authored by Li et al. [19] and Zhang et al. [20], they used a nanochannel alumina as the template and grew successfully a hexagonally ordered CNT array. Ren et al. grew vertically aligned CNT array in a plasma-enhanced chemical vapor deposition (PECVD) environment [5].

In the CVD process, the formation of catalyst particles plays a key role for growing vertically aligned CNTs. Substrates pre-coated with multilayer metal catalyst were used in many studies [6–9,21]. Nano-particles form when the pre-coated iron film is subjected to thermal annealing. The size of nano-particles was affected significantly by the thickness of iron film, which influenced the CNT diameter in the CVD process [17]. Catalyst with different compositions, which can be obtained by coating different transition metals on substrate, yields different CNT morphologies.

Various substrates including silicon, silica, glass [5], and quartz [18,22] have been reported for the growth of aligned CNTs. The silicide layer on silicon substrate is a critical parameter to influence the growth of CNTs. A silica layer with the thickness in the range of 5–6 nm is required to produce aligned CNTs, when the silica thickness increases up to 24 nm, the growth rate becomes saturated [16].

This work proposes a special design in the CVD process for synthesizing long CNTs. In this study, vertically aligned CNTs were synthesized using acetylene as the carbon source. CNT lengths and its growth rates were measured for the CNTs grown on lithographically patterned silicon/silica

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doi:10.1016/j.surfcoat.2005.07.016

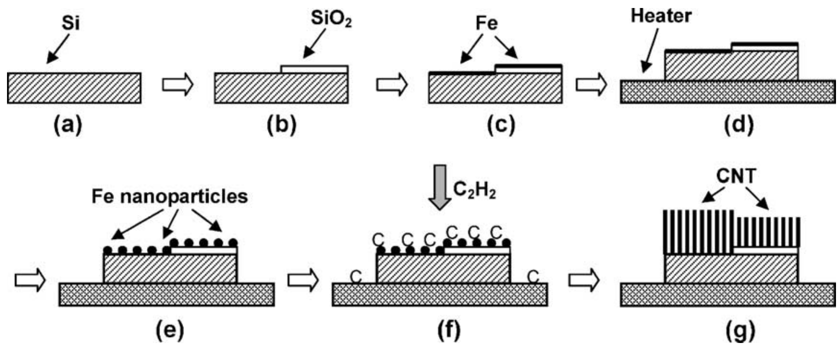

Fig. 1. The schematic sketch of the vertically aligned CNT process. (a) Si wafer with the size of 5×5 mm^2. (b) Formation of silica film (500 nm) on the Si substrate. (c) Fe thin films from 0.3 to 3.0 nm were coated. (d) The as-prepared substrate placed on the heater of the RHCS in the chamber. (e) Formation of nano-catalysts from iron film at 700–900 °C. (f) Acetylene acted as carbon source was introduced into the chamber. (g) The vertically aligned CNTs were synthesized on the silicon/silica patterned substrate.

substrate. An extremely high growth rate of 50.0 μm/min and an ultra long CNT array near 500 μm were achieved.

2. Experimental

The processes for the heat treatment of substrate and the growth of vertically aligned CNT array are shown in Fig. 1. It involves the formation of silica film (~ 500 nm) on silicon substrate (5×5 mm^2) by thermal annealing and photo lithograph, as shown in Fig. 1(a) and 1(b). An iron thin film with the thickness between 0.3 and 3.0 nm was coated onto the patterned substrate by DC sputtering at 100 W, as shown in Fig. 1(c). The substrate was then placed on the heater of the RHCS system, as shown in Fig. 1(d) in a high vacuum chamber (~ 10^{-6} Torr). The heater fixed in the feedthrough was made of Ta foil and wire. The heater can be heated from room temperature to 900 °C within 20 s and cooled down from 900 °C to 250 °C within 25 s. In the RHCS CVD chamber, the time for thermal annealing and for CNT growth can be controlled. The processing temperature was measured using a thermo-couple which was welded on the heater.

The nano-catalysts, as shown in Fig. 1(e), were converted from the pre-coated iron thin film at 700–900 °C. In the process, a low pressure of 10 Torr and a flow rate of 30 sccm of 10% H_2/Ar mixture were maintained. Acetylene which acted as the carbon source was introduced into the chamber at a flow rate of 60 sccm, as shown in Fig. 1(f). The morphologies and the structure of the synthesized CNTs, as shown schematically in Fig. 1(g), were examined by the field emission scanning electron microscope (FESEM, JEOL 6500F) and the high resolution transmission electron microscope (HRTEM, JEOL 2010), respectively.

3. Results and discussion

The substrate pre-coated with iron was placed on the heater in the RHCS CVD chamber, and the inlet for carbon source was located above the substrate. It is expected that

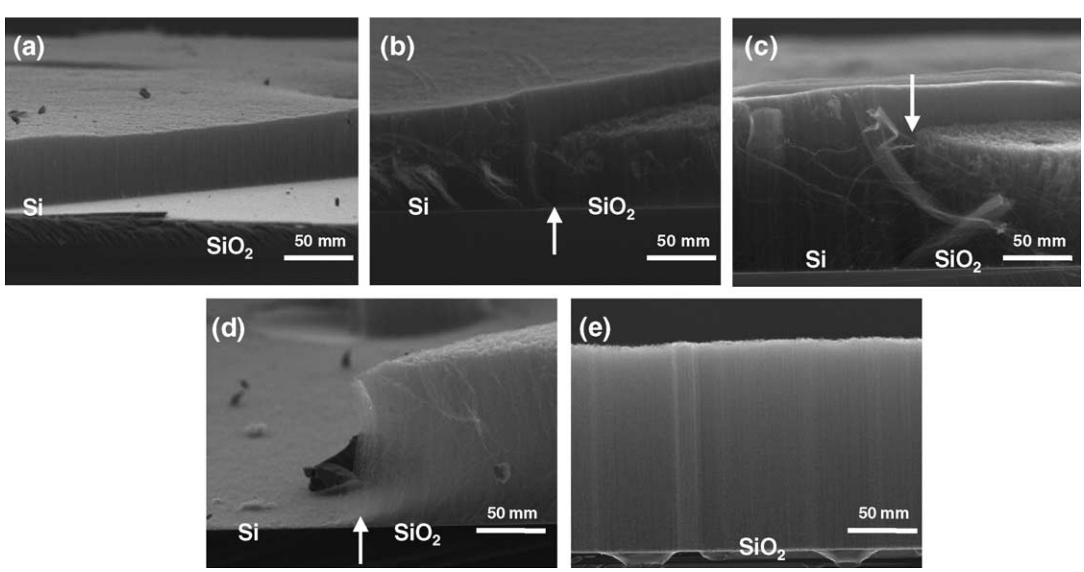

Fig. 2. The FESEM images of vertically aligned CNTs which were obtained at the temperatures of (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, and (e) 900 °C.