



# Catalyst design for high-density and low-temperature CNT synthesis on conductive Ti silicide substrate



Suwen Li<sup>a,\*</sup>, Changjian Zhou<sup>b</sup>, Salahuddin Raju<sup>a</sup>, Mansun Chan<sup>a</sup>

<sup>a</sup>Department of Electronic and Computer Engineering, Hong Kong University of Science and Technology, Kowloon, Hong Kong

<sup>b</sup>South China University of Technology, Guangzhou 510641, PR China

## ARTICLE INFO

### Article history:

Received 17 October 2016

Accepted 3 January 2017

Available online xxxx

### Keywords:

Carbon nanotubes

Nanoparticles

Ni multilayer catalyst

High density

Base growth mode

## ABSTRACT

A multilayer (Ni/Al/Ni) catalyst design is proposed to synthesize high-density carbon nanotubes (CNTs) on a conductive titanium silicide substrate. The Al intermediate layer immobilizes the Ni catalyst on the substrate during nanoparticle formation by interacting with the top and bottom Ni catalyst film, suppressing the diffusion of Ni into silicide and sintering of the Ni nanoparticles, as evidenced by secondary ion mass spectroscopy and atomic force microscopy analysis. Owing to the stable, high-density and evenly distributed nanoparticle catalysts with the multilayer catalyst design, we have synthesized vertically aligned CNTs with a density of  $2.0 \times 10^{10}/\text{cm}^2$  and an average 50 walls per CNT. The CNT density using the Ni/Al/Ni catalyst is three times higher than that with the pure Ni catalyst. Furthermore, the proposed catalyst design enables CNT synthesis at a temperatures as low as 350 °C. The synthesized CNTs show Ohmic contact with Ti silicide, suggesting the catalyst design is promising for CNT applications on conductive substrates, especially for interconnect applications.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to carbon nanotubes' (CNTs') outstanding electrical, mechanical and thermal properties, they have promising applications as interconnects in integrated circuits, thermal interface materials and supercapacitors [1–3], which require CNT synthesis on conductive substrates for an electrically conductive path. Especially, to apply CNTs as vertical interconnects, high-density vertically aligned CNTs on conductive substrates are required to provide conductivity comparable to that of the current copper-based interconnects. To this end, the conductive substrate and catalyst used to synthesize CNTs need to be carefully chosen and designed.

High-density CNT synthesis on conductive substrates is known to be more difficult than on insulating substrates, such as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , which have low surface energy. The main reason is that the catalyst nanoparticles used to synthesize CNTs are difficult to form on high surface energy conductive materials. An additional  $\text{Al}_2\text{O}_3$  or oxidized Al layer below the catalyst has been used to enhance catalyst nanoparticle formation on conductive substrates [4–7].

However, the insulating nature of  $\text{Al}_2\text{O}_3$  will eventually hinder CNT's conductivity and its contact with the substrate.

Another issue is that the most widely used Fe catalyst is contagious, which limits its usage for CNT interconnects in CMOS technology. Compared to the Fe catalyst, Ni catalyst is CMOS compatible. Even though many theoretical studies and in-situ observations of CNT growth with the Ni catalyst have been done to reveal the growth mechanism, the use of Ni catalyst to synthesize vertically aligned CNTs on conductive substrates is still less explored compared to Fe and Co catalysts [8–12]. And CNTs grown with the Ni catalyst on substrates such as Si and TiN are of relatively low density due to Ni diffusion and aggregation as well as Ni nanoparticle encapsulation [13–15]. Therefore it is necessary to explore the CNT growth mechanism using the Ni catalyst and enhance Ni's catalytic properties.

In this work, we use a Ni-based catalyst without an additional insulating layer to synthesize vertically aligned high-density CNTs on a titanium silicide conductive substrate. Ti silicide adopted in CMOS technology, is highly conductive and thermally stable and is the favored contact with Si and other materials. The proposed catalyst design suppresses the Ni catalyst diffusion and sintering by altering the interaction between the catalyst and substrate, thus improving the CNT density and uniformity. The catalyst nanoparticle formation and the synthesized CNTs are systematically characterized to reveal the growth mechanism.

\* Corresponding author.

E-mail addresses: [sliao@ust.hk](mailto:sliao@ust.hk) (S. Li), [zhoucj@scut.edu.cn](mailto:zhoucj@scut.edu.cn) (C. Zhou).

## 2. Methods

To form the catalyst, 4 nm Ni was deposited by electron beam evaporation on the Ti silicide substrate at a rate of  $0.2 \text{ \AA/s}$  under a pressure around  $3.0 \times 10^{-7}$  Torr. The samples were then transferred into a CNT plasma enhanced chemical vapor deposition (PECVD) chamber (Seki Technotron Corp. AX5200M) and annealed at  $650 \text{ }^\circ\text{C}$  with  $\text{H}_2:\text{N}_2 = 3:1$  at 2.8 Torr to form nanoparticles as the catalyst. After 10 min, methane ( $\text{CH}_4$ ) was introduced at 35 sccm as the carbon source with 200 W plasma power for 1 min. Finally, the sample was cooled down to room temperature in  $\text{H}_2$  atmosphere.

The two major problems in using the pure Ni catalyst are the penetration of Ni atoms through the silicide and non-uniform nanoparticle diameters due to sintering, as shown in the schematic in Fig. 1 (a). In order to improve the density and uniformity of the grown CNTs, a multilayer catalyst was designed with an Al intermediate layer to change the surface energy of the Ni nanoparticles to prevent sintering and diffusion as shown in Fig. 1 (b). The Al intermediate layer has to be thin enough to maintain the catalytic property of the Ni nanoparticles for CNT growth. In the multilayer catalyst preparation, a 1 nm Al layer was inserted into the Ni catalyst to form a Ni/Al/Ni (2 nm/1 nm/2 nm) multilayer structure. The total thickness of the Ni was kept at 4 nm, split into a 2 nm top and 2 nm bottom layer to keep the same amount of the catalyst for comparison. The deposition of the Ni and Al was done in the same chamber without breaking the vacuum to avoid contamination and oxidation of the film. The nanoparticle formation and CNT growth processes in the CNT PECVD chamber were kept the same as with the pure Ni catalyst. In the low temperature CNT synthesis, nanoparticle formation and CNT growth were performed at  $350 \text{ }^\circ\text{C}$  with a thinner multilayer catalyst Ni/Al/Ni (1 nm/0.5 nm/1 nm).

Nanoparticle samples were prepared by annealing the same catalyst films at  $650 \text{ }^\circ\text{C}$  under the same conditions, except that the  $\text{CH}_4$  gas and plasma were not introduced. The annealed film was characterized after cooling to room temperature. The nanoparticle morphology and distribution were characterized by atomic force microscopy (AFM) (Bruker Dimension Icon, tapping mode). The amount of Ni on the surface and diffusion into the silicide was characterized with time-of-flight secondary ion mass spectroscopy (TOE SIMS) (ION-TOF GmbH).

The morphology and density of the synthesized CNTs were characterized by scanning electron microscopy (SEM) (Hitachi S-4800). The growth mode and wall distribution were examined with a transmission electron microscope (TEM) (JEOL Model JEM-2100F). TEM energy dispersive X-ray spectrometry (EDS) was employed

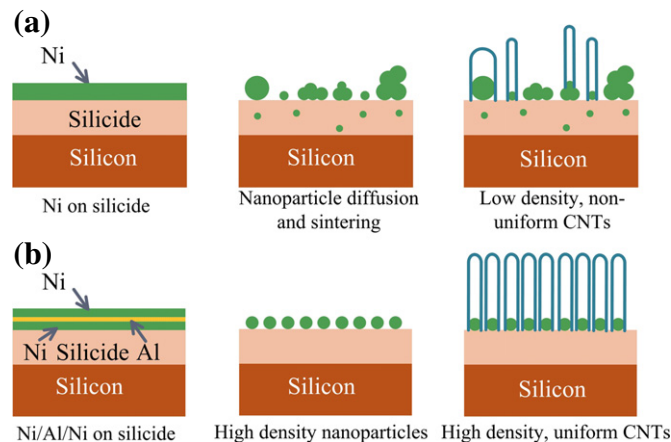


Fig. 1. Schematics showing the catalyst deposition, nanoparticle formation upon annealing, and CNT growth on Ti silicide with (a) Ni catalyst and (b) Ni/Al/Ni multilayer catalyst.

to analyze the atomic composition of the Ni nanoparticle. For the electrical measurement, we first fabricated a  $3\mu\text{m} \times 3\mu\text{m}$  oxide insulated CNT vertical interconnect on Ti silicide. Dielectric filling by atomic layer deposition (ALD) and polishing were then performed to planarize the surface. After metalization, the electrical properties of the formed CNT interconnect were characterized with an Agilent 4156C Precision Semiconductor Parameter Analyzer.

## 3. Results and discussion

### 3.1. Prevention of catalyst diffusion and sintering

The role of the thin Al layer in the multilayer catalyst was investigated by measuring and comparing the depth profiles of the catalyst films annealed from a Ni sample and a Ni/Al/Ni multilayer sample. The Ni profile of both samples shows higher Ni concentration near the source at the surface, with the Ni signal decreasing towards the substrate (Fig. 2). However, with the pure Ni sample (Fig. 2 (a)), there is a significant amount of Ni inside the silicide, which confirms the diffusion of Ni catalyst through the Ti silicide. This is consistent with the fact that Ni nanoparticles are not stable on conductive substrates. This kind of diffusion can lead to undesirable traces of Ni in the silicon, as well as a reduced amount of the catalyst to form the nanoparticles. In comparison, with the Ni/Al/Ni catalyst

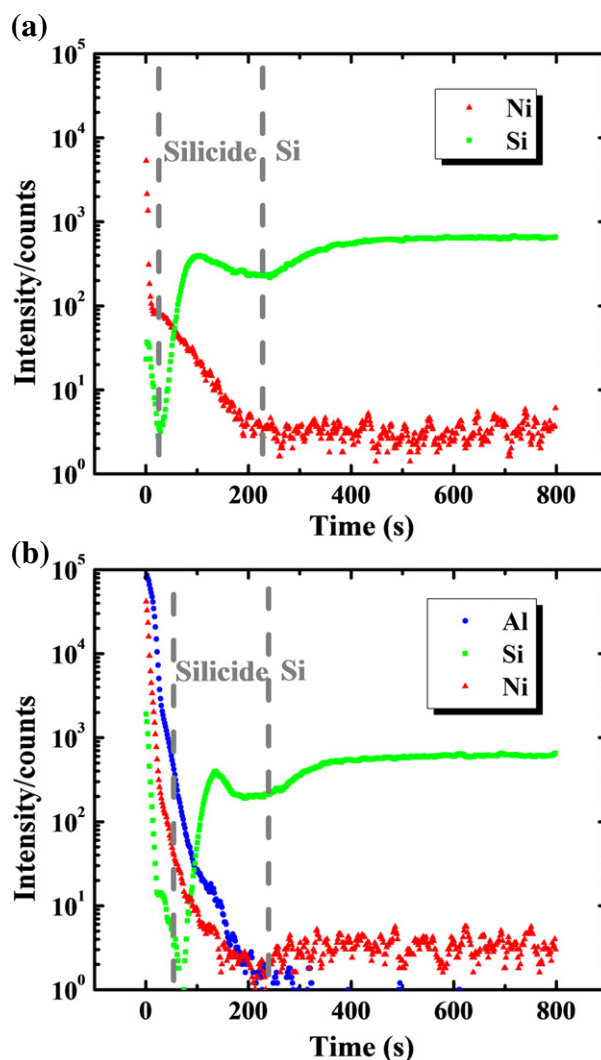


Fig. 2. SIMS depth profiles of nanoparticle samples annealed at  $650 \text{ }^\circ\text{C}$  from (a) 4 nm Ni catalyst and (b) Ni/Al/Ni (2 nm/1 nm/2 nm) multilayer catalyst.

Download English Version:

<https://daneshyari.com/en/article/5000750>

Download Persian Version:

<https://daneshyari.com/article/5000750>

[Daneshyari.com](https://daneshyari.com)