Simple and engineered process yielding carbon nanotube arrays with $1.2 \times 10^{13} \text{ cm}^{-2}$ wall density on conductive underlayer at 400 °C

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ABSTRACT

A simple process is presented that realizes carbon nanotube (CNT) arrays that meet the process and structure requirements for use in large-scale integrated circuits. Ni particles are formed densely on a conductive TiN layer on SiO₂/Si substrates through nucleation and growth by sputtering, which was stopped prior to percolation of the Ni particles. Ni particles as dense as $2.8 \times 10^{12} \text{ cm}^{-2}$ were formed after annealing at 400 °C and chemical vapor deposition (CVD) was carried out at 400 °C by feeding C₂H₂ at partial pressures as low as 0.13–1.3 Pa so as not to kill the catalyst. Scanning electron microscopy with energy dispersive X-ray spectroscopy revealed the mass density of the arrays to be as high as 1.1 g cm⁻³. High resolution transmission electron microscopy showed the densely packed CNTs

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with an average wall number of eight. Atomic force microscopy of the root of the CNT arrays transferred to a SiO₂/Si substrate enabled direct counting of individual CNTs, revealing areal densities of CNTs and CNT walls as high as 1.5×10^{12} and $1.2 \times 10^{13} \text{ cm}^{-2}$, respectively. The simple process, using conventional sputtering and CVD apparatus, with carefully engineered conditions offers a route for practical application of CNTs.

1. Introduction

Vertically aligned, dense carbon nanotube (CNT) arrays [1–4] have gathered interest because of their potential application in nanoscale electronic devices [5,6]. In particular, via interconnects in large-scale integrated circuits (LSIs) using densely packed CNT arrays are attractive because CNTs can carry electric current at a high current density ($\sim 10^9$ A cm⁻²) [7] without scattering at the sidewalls of the interconnects [8]. This cannot be achieved by currently available Cu interconnects. CNTs also possess an excellent conduction channel for each wall and, therefore, putting CNT walls as much as possible in the via holes becomes a key issue for realizing interconnects with low resistivity and high current-carrying capacity.

For perfect, closely packed, single-wall CNT (SWCNT) arrays, a high number density of $\sim 1 \times 10^{14}$ cm⁻² is expected. However, SWCNTs normally contain a larger fraction of semiconducting tubes than metallic tubes (semiconducting tubes:metallic tubes $\approx 2:1$ for SWCNTs of random chirality) [9,10], making the situation unsuitable for electrical conduction. Furthermore, it is technologically difficult to realize 1-nm-sized catalyst particles at a number density of $\sim 1 \times 10^{14}$ cm⁻² because particles can have a spacing much smaller than 1 nm and such small particles easily aggregate. Indeed, millimeter-tall dense SWCNT arrays are commonly very porous (porosity >0.9) with an areal density of $\sim 1 \times 10^{12}$ cm⁻² and a mass density of 0.03–0.07 g cm⁻³ [3,11]. However, multi-wall CNTs (MWCNTs) always exhibit metallic properties as a result of the interaction between neighboring walls [12]. For example, an array of MWCNTs with a 4-nm diameter, five walls, and 4×10^{12} cm⁻² areal density has a high wall density of 2×10^{13} cm⁻² while an array of catalyst particles with a diameter of 4 nm and areal density of 4×10^{12} cm⁻² can have a spacing ≥ 1 nm. Thus, such structures, i.e., dense arrays of MWCNTs, are good candidates for interconnects.

Production process is also important. Vertically aligned CNT arrays are often formed at high CVD temperatures of 600–800 °C on insulating underlayers such as Al₂O₃

[1–4,11,13,14]. However, CNTs should be synthesized on a conductive layer to be useful as interconnects, and at low temperatures (~ 400 °C) to avoid any damage to LSIs. The three requirements, i.e., high wall density $\sim 10^{13}$ cm $^{-3}$, low CVD temperature ≤ 400 °C, and being on a conductive underlayer need to be satisfied to realize the practical application of CNT-based via interconnects in LSIs.

Awano and coworkers have pioneered work into CNT interconnects [15–18]. They developed a cluster deposition method [16] in which catalyst particles are formed by laser ablation, size selected, and then introduced into the bottom of the via holes as a cluster beam. This approach can realize the growth of MWCNT arrays at a density of $\sim 3 \times 10^{11}$ cm $^{-2}$ from the bottom of the via holes at the low temperature of 450 °C [17]. Later, they developed a multi-step growth method [18], whereby in the first step, a H $_2$ or Ar plasma is applied to a Co catalyst layer on a conductive TiN/Ta barrier layer on Cu to induce Co particle formation at 25–260 °C. A CH $_4$ /H $_2$ plasma is then applied to nucleate CNTs at 170–350 °C, before finally a CH $_4$ /H $_2$ plasma is applied to grow CNTs at 450–600 °C. By observing the cross-section of the CNTs using a scanning electron microscope (SEM), they estimated the areal density to be as high as $\sim 1 \times 10^{12}$ cm $^{-2}$ for the CNT arrays produced via this multi-step process at 450 °C. Zhong, Robertson, and coworkers have also extensively researched in this area [19–21]. They used an Al $_2$ O $_3$ /Fe/Al $_2$ O $_3$ sandwich catalyst [3] and grew SWCNTs, reporting on high-density SWCNT arrays [20]. By assuming the absence of carbon byproducts and the SWCNTs to be perfectly straight, they estimated, indirectly from the film weight and the SWCNT diameter, the areal density of these SWCNTs to be as high as $\sim 1.64 \times 10^{13}$ cm $^{-2}$. Because the SWCNT arrays were grown on an insulator at a CVD temperature as high as 700 °C, this method does not meet the requirements for via interconnects in LSIs. Recently, Sugime et al. reported on MWCNT arrays with a mass density as high as 1.6 g cm $^{-3}$ using the Co-Mo co-catalyst on a conductive Ti-coated Cu layer at a rather low CVD temperature of 450 °C [21]. This

achievement is closer to the application requirements and, thus, encouraging, but the areal density of CNTs and their walls have not yet been determined. Both the growth of CNTs that meet the process and structure requirements (≤ 400 °C, $\geq 1 \times 10^{13}$ walls cm^{-2} , on a conductive underlayer) and the direct determination of the areal density of CNTs and their walls remain challenges.

In this work, we propose a simple process that meets the process requirements and introduce a detailed structure analysis that directly illustrates that the CNT and wall densities achieve the structure requirements.

2. Experimental

Si wafer with a 50-nm-thick thermal oxide (SiO_2) layer was cleaned using a 3:1 solution of sulfuric acid (H_2SO_4) (98 wt%) and aqueous hydrogen peroxide (H_2O_2) (30 wt%) and used as the substrate. A 5-nm-thick TiN conductive underlayer was deposited by radio frequency sputtering with a Ti target in N_2/Ar , and then Ni with a 0.6-nm nominal thickness was immediately deposited onto TiN by direct current sputtering with an Ni target in Ar without breaking the vacuum. A magnetron sputtering apparatus (MPS-2000HC2S; ULVAC, Chigasaki, Japan) with a base pressure $< 2 \times 10^{-6}$ Pa was used for both depositions. Various deposition conditions were investigated for Ni: temperatures (room temperature and 400 °C), deposition rates (8.1 pm s^{-1} and 34 pm s^{-1}), and substrate bias (0 and -20 V). Deposition rates were controlled by changing the discharge power between 10 and 50 W for the 2-inch Ni target.

CNTs were grown by CVD using nominally 0.6-nm-thick Ni catalyst deposited on 5-nm-thick TiN at 400 °C and 8.1 pm s^{-1} with -20 V substrate bias. After the catalyst deposition process, substrates were set in a tubular quartz glass, CVD reactor (34-mm inner diameter, 300-mm length) [19], and annealed with pure H_2 (30 sccm) at 1.3 kPa during

heating to 400 °C and keeping at this temperature for 8 min. Finally, CVD was carried out at a rate of 180 sccm for 5–60 min by switching the gas to 0.13–1.3 Pa C₂H₂ with Ar balance gas at 0.27 kPa.

The catalysts before and after annealing were analyzed by atomic force microscopy (AFM; SPM 9600 and 9700; Shimadzu, Kyoto, Japan) and the number densities of the particles were derived from the AFM images. The resulting CNTs were characterized using a field emission SEM (S-4800; Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS; EDAX Genesis; AMETEK, Berwyn, PA, USA) and high-resolution transmission electron microscopy (HRTEM; JEM-2800 and JEM-2100F; JEOL, Akishima, Japan). Some CNT films were separated from the substrate by etching the Ni/TiN/SiO₂ layer using HF (25 wt%) solution and transferred to Si substrates or TEM microgrids with their bottom up (upside down). These were analyzed by SEM and AFM to take the bottom view images and by TEM to take the transmittance images perpendicular to the film surface. The absence of Ni/TiN/SiO₂ at the roots of the transferred CNT arrays was confirmed by X-ray photoelectron spectroscopy (XPS; PHI Versa Probe II; ULVAC-PHI, Chigasaki, Japan) using a monochromatized Al K α X-ray source and a 45° detection angle. The amount of carbon (g cm⁻²) was determined by the C to Si peak area ratios by SEM-EDS analysis at an acceleration voltage of 5 kV, and using the film thickness (cm) to determine the mass density of the CNT films (g cm⁻³). Sputtered carbon films on Si substrates were used as a reference for the EDS analysis (supplementary data, Fig. S1), where the density was determined by X-ray reflection measurement (ATX-G; Rigaku, Akishima, Japan) to be 1.66 g cm⁻³.

3. Results and discussion

3.1 Preparation of dense catalyst particles on a conductive underlayer

We first designed the catalyst preparation method. As shown in Fig. 1a,b, there are two main approaches for catalyst preparation. One is to pre-form the catalyst particles and then deposit the particles on the substrate, such as by the cluster deposition method [16], and wet coating of the colloidal catalyst particles [22]. When we attempt to deposit the catalyst densely, catalyst particles inherently deposit on the catalyst particles and/or aggregate (Fig. 1a) unless some countermeasure, such as the use of oxide particles, is applied [22]. The second approach is to pre-form the catalyst layer on substrates and then transform the layer into particles. Although extensive efforts have been made to form catalysts at high densities using plasma treatment [18–20], spaces inherently form between the catalyst particles (Fig. 1b). Therefore, we herein propose an alternative approach, namely direct nucleation and growth of catalyst particles on substrates (Fig. 1c). When we sputter catalyst on heated substrates, catalyst adatoms diffuse over the surface, attach to each other, and nucleate particles (islands). As deposition proceeds, nucleated particles grow larger and get percolated. If we halt deposition prior to percolation, we may obtain catalyst particles that are densely packed with minimal space between them. Even at ambient temperature, metal particles nucleate and grow during sputtering on substrates [23,24], but their density is too high to retain the high density upon heating (Fig. 1d). Preparing catalyst particles at high, but not too high, density should be key (Fig. 1e).

Fig. 1 – Approaches for preparation of catalyst particle arrays on substrates. (a) Pre-forming catalyst particles and then depositing the particles on the substrate. (b) Pre-forming the catalyst layer on substrates and then transforming the layer into particles. (c) Directly nucleating and growing catalyst particles on substrates. (d,e) Our strategy for maintaining catalyst particles at high densities during CVD.

Based on this concept, we carefully examined the catalyst preparation. The requirement of low CVD temperature is beneficial for preparation of dense catalyst particles on conductive underlayers because both catalyst deactivation as a result of alloying with the underlayer and coarsening through Ostwald ripening [25,26] can be prevented at low temperatures. We selected TiN [18], which is frequently used as a barrier material in LSIs, as the conductive underlayer and deposited Ni onto it.

Fig. 2 shows the AFM images obtained of the nominally 0.6-nm-thick Ni deposited onto 5-nm-thick TiN on SiO₂/Si substrates. Of the systems studied herein, Ni deposited at ambient pressure and at a high rate of 34 pm s⁻¹ had the finest structure at deposition but had the most

pronounced particulate structure with a particle number density of $1.2 \times 10^{12} \text{ cm}^{-2}$ after annealing under H_2/Ar at 400°C for 10 min (Fig. 2a). An increased deposition temperature of 400°C , which enhances the surface diffusion of Ni, yielded a rougher structure as deposited but kept the finer particulate structure with the increased particle number density of $1.6 \times 10^{12} \text{ cm}^{-2}$ after annealing (Fig. 2b). A similar effect was observed for a decreased deposition rate of 8.1 pm s^{-1} , which allows Ni adatoms to diffuse for a longer period of time, yielding particles at $1.9 \times 10^{12} \text{ cm}^{-2}$ after annealing (Fig. 2c). The combination of high deposition temperature (400°C) with low deposition rate (8.1 pm s^{-1}) realized even denser particles at $2.4 \times 10^{12} \text{ cm}^{-2}$ (Fig. 2d). Finally, application of a substrate bias voltage of -20 V , which further enhances the surface diffusion of Ni by irradiation of cationic species [27], in addition to the high deposition temperature and low deposition rate, made particles with the highest density of $2.8 \times 10^{12} \text{ cm}^{-2}$ after annealing (Fig. 2e). The particle arrays having the highest (Fig. 2a) and lowest densities (Fig. 2e) as deposited, which yield particles at the lowest and highest densities, respectively, after annealing, are shown with a modified height scale in Fig. 2f,g for comparison. It should be noted that catalysts for CNT growth are often deposited at room temperature and high deposition rates, which correspond to the conditions for Fig. 2a. This may be one reason why catalyst particles formed from a sputtered layer by annealing are often not particularly dense (around $1 \times 10^{12} \text{ cm}^{-2}$) [11,28]. These results support the concept that to yield dense particle arrays after annealing (and thus prior to CVD), the initial Ni layer should be formed at a moderate island density by promoting the surface diffusion of Ni.

Of course, excess promotion of surface diffusion causes as-deposited islands to be too large and sparse, which is unsuitable for CNT growth. If the as-deposited catalyst shows an isolated particulate structure, surface diffusion needs be suppressed. In contrast, if the as-deposited catalyst shows a continuous film structure, surface diffusion needs to be promoted. Optimization of surface diffusion and nominal catalyst thickness are important for

providing dense catalyst particle arrays. The 0.6-nm-thick Ni catalyst deposited on 5-nm-thick TiN at 400 °C and 8.1 pm s^{-1} with -20 V substrate bias (Fig. 2e) was used to grow CNTs by CVD in the following sections.

Fig. 2 – (a–e) AFM images of Ni particles deposited at different temperatures and deposition rates. The number densities of the Ni particles are shown in the images after annealing at 400 °C for 10 min. (f,g) The AFM images shown at a magnified height scale. (f) and (g) are of the same images as those as deposited (as sputtered) in (a) and (e), respectively. The scale bar for the lateral dimension in (a) applies for all images. And the scale bar for the height in (d) applies for the images (a–e).

3.2 Growth of CNT arrays using the dense catalyst particle arrays at 400 °C

Various carbon containing species, such as C_2H_2 [26,28,29], C_2H_4 [2,4], and $\text{C}_2\text{H}_5\text{OH}$ [10], can be used as feedstock for millimeter-tall, vertically aligned CNT arrays. However, C_2H_2 directly fed or forming through the decomposition of hydrocarbon/alcohol has been proven to be an efficient direct precursor for growth of such arrays [30]. Coarsening of catalyst particles

through Ostwald ripening and carbonization of catalyst particles as a result of the excess carbon feed are important deactivation mechanisms. While the former is suppressed at lower temperature, the latter gets more significant at lower temperature and, thus, the C_2H_2 should be fed at lower partial pressures for lower CVD temperatures [26]. Hence, we fed 0.13–1.3 Pa C_2H_2 at 400 °C, which is two to three orders of magnitude lower than that for the millimeter-tall CNT arrays at 800 °C in previous studies [26,28,29]. Fig. 3 shows cross-sectional SEM images of the CNT arrays grown on the conductive TiN underlayer for different growth times and C_2H_2 partial pressures. CNTs grew in vertically aligned arrays under all of the conditions examined. CNTs were shorter for the lower C_2H_2 pressures at the initial stage of 5–10 min, while they became similar in height at the later stages (30–60 min). There are some differences in the surface smoothness obtained at these different conditions: CNT arrays had a rough surface with 0.13 Pa C_2H_2 (Fig. 3a–d), whereas they had a smooth surface with 1.3 Pa C_2H_2 (Fig. 3e–h). We also examined the growth of CNT arrays using C_2H_2 at even lower pressure (0.04 Pa), and found that CNT arrays grew taller over time until 60 min, even though their alignments and mass densities were not desirable (Fig. S2). These results show that CNTs nucleate more quickly and grow faster but stop growing earlier for higher pressure C_2H_2 feed.

Fig. 3 – Cross-sectional SEM images of CNTs grown by Ni catalyst on TiN at 400 °C from (a–d) 0.13 Pa and (e–h) 1.3 Pa C₂H₂ for (a,e) 5, (b,f) 10, (c,g) 30, and (d,h) 60 min.

Next, we carefully characterized the average height, areal density, and mass density of the CNT arrays for growth times of 5–30 min (when CNTs keep growing) (Fig. 4). The height of the CNT arrays continuously increased with growth time until about 30 min for both the 0.13 and 1.3 Pa C₂H₂ pressures (Fig. 4a). However, the amount of carbon almost stopped increasing after a growth time of 20 min for the higher C₂H₂ pressure (1.3 Pa) (Fig. 4b). This result suggests that the significant fraction of Ni catalyst particles were deactivated within 20 min with 1.3 Pa C₂H₂, and the CNTs are growing at a low density from 20 to 30 min at the bottom of the CNT array, lifting up the pre-formed dense array. In contrast, the amount of carbon increased over the period of 20–25 min for the lower C₂H₂ pressure (0.13 Pa) (Fig. 4b), indicating that a significant fraction of the catalyst particles remained active for 20 min or more. From the CNT height and amount of carbon, we calculated the mass density of the CNT arrays. It was initially as high as 1.0 g cm⁻³ (5–10 min) but decreased to ~0.75 g cm⁻³ after 30 min for both 0.13 and 1.3 Pa C₂H₂ (Fig. 4c).

Fig. 4 – (a) Height, (b) amount of carbon, and (c) mass density of the CNT arrays grown by Ni catalyst on TiN at 400 °C from 0.13 Pa (●) and 1.3 Pa (○) C₂H₂. The mass densities of the CNT arrays were initially 0.7–1.1 g cm⁻³ and decreased to ~0.75 g cm⁻³ after 30 min for both 0.13 and 1.3 Pa C₂H₂.

3.3 Direct counting of CNTs and their walls in the arrays

Of key importance is the areal density of the CNT walls, which provide the electrical conduction channels; however, this has not yet been directly evaluated. CNT arrays commonly have a disordered part at their top and, thus, it is difficult to count the number of CNTs within the array. Here, we realized the direct observation of the CNT roots and CNT walls within the CNT arrays by preparing upside-down CNT films on different substrates. The CNT arrays on the growth substrates were lifted off by etching the Ni/TiN/SiO₂ layer and then transferred to TEM microgrids (or Si substrates) with their roots up, as shown in Fig. 5a. We analyzed the bottom surface of a CNT array by XPS (Fig. S3) and confirmed that the Ni/TiN/SiO₂ layer was removed almost completely from the bottom surface. Such transfer was possible for the CNT arrays as dense as ~1 g cm⁻³ due to its solid nature (Fig. S4a,b) whereas was impossible for the CNT arrays with a lower density (0.3 g cm⁻³) synthesized at 500 °C (Fig. S4c). Fig. 5b shows the SEM image of the CNT array transferred to the microgrid. The few-μm-wide cracks (A,B) were formed in the film by being torn and lifted up

on one side, which match the counterpart remaining on the microgrid. The sub- μm -wide cracks (C,D) can also be seen, and these might originate from the shrinkage of the CNT arrays upon wetting and drying [31]. Overall, the transferred films showed minimal shrinkage (<few %) owing to the mass density being as high as $\sim 1 \text{ g cm}^{-3}$. Fig. 5c shows an enlarged image of the lifted-up part of the CNT array in Fig. 5b. We can clearly see the upside-down structure in Fig. 5c: rough top surface at the lower left side and smooth bottom surface at the upper right side. Fig. 5d–g shows the bottom-view SEM images of CNT arrays grown for 5 and 30 min. CNT roots are densely packed for the arrays grown for 5 min for both C_2H_2 pressures (d,f), whereas many voids were observed in the arrays grown for 25–30 min for both C_2H_2 pressures (e,g). The increasing number of CNTs stop growing over time, and these are lifted up by the growing CNTs, resulting in the void formation at their root and decreasing mass density (Fig. 3c). When compared with the AFM image of the catalyst particles (Fig. 5h), the round shapes in the SEM images (d–g) seem somewhat larger. As discussed later using AFM images, the round shapes correspond to the roots not of the individual CNTs but CNT bundles in these SEM images.

Fig. 5 – (a) Schematic of the transfer process of the CNT arrays from the growth substrates to TEM microgrids; the Ni/TiN/SiO₂ layer in between the Si substrate and the CNT array was etched by HF (25 wt%) solution, and the CNT arrays floating in the solution were captured by the microgrid. (b,c) Typical SEM images of the CNT array transferred to the TEM microgrid. (d–g) High-magnification, bottom-view SEM images of the CNT arrays grown by Ni catalyst on TiN at 400 °C from (d,e) 0.13 and (f,g) 1.3 Pa

C_2H_2 for (d,f) 5, (e) 25, and (g) 30 min. (h) The same AFM image of Ni catalyst particles as Fig. 2e is shown for comparison. The Ni particles were prepared under the same conditions as for Fig. 2e ($400\text{ }^\circ\text{C}$ and 8.1 pm s^{-1} with -20 V bias voltage) and used to grow the CNTs in (d–g).

Next, we carried out further analysis on the CNT arrays on the TEM microgrids using TEM (Fig. 6). To make electrons transmit through CNT arrays as dense as $\sim 1 \text{ g cm}^{-3}$, the CVD time was adjusted to make CNT arrays as thin as $\sim 100 \text{ nm}$ (Fig. 6a,c). In the plan-view HRTEM images of the CNT arrays (Fig. 6b,d), densely packed concentric circles (shown by white arrows) can be seen, similar in appearance to the annual growth rings of trees, corresponding to individual MWCNTs. Individual MWCNTs grown from 0.13 Pa (Fig. 6b) and 1.3 Pa (Fig. 6d) C_2H_2 were 7 and 8 nm in average diameter, respectively, and both had an average of 8 walls. The diameter and number of walls of individual CNTs were determined mainly by the structure of the catalyst particles used (Fig. 2e), although the CNT diameter may increase slightly with the increase in C_2H_2 partial pressure.

Fig. 6 – Cross-sectional SEM (a,c) and plan-view HRTEM (b,d) images of the CNT arrays grown at 400 °C from 0.13 (a,b) and 1.3 (c,d) Pa C_2H_2 using the Ni/TiN catalyst under the same conditions as in Fig. 2e (400 °C, 8.1 pm s^{-1} , and -20 V bias voltage). The CNT arrays were transferred to the TEM microgrids by the method shown in Fig. 5a.

Growth of a CNT array at an intermediate C_2H_2 pressure (0.40 Pa) for 7 min was also investigated (Fig. 7). Their height and density, determined by SEM and EDS analyses (Fig. 7a,b), were approximately 140 nm and 1.1 g cm^{-3} , respectively, which are similar but somewhat taller and denser than the CNT array grown at 0.13 Pa for 10 min (Fig. 4). We carefully analyzed the root of this CNT array by bottom-view AFM (Fig. 7c–e). The low-magnification image (Fig. 7c) shows that the film had the densely packed region at 92% with the void regions at 8%, which may have been caused by the solution-base transfer process discussed for Fig. 5. The densely packed regions (Fig. 7d,e) were observed at a higher magnification, which provides the clear image of the roots of individual CNTs. The number of CNTs were $1.7 \times 10^{12} \text{ cm}^{-2}$ (Fig. 7d) and $1.6 \times 10^{12} \text{ cm}^{-2}$ (Fig. 7e). By considering the coverage of the densely packed region (92%), we determined the number density of CNTs for the whole region to be $1.5 \times 10^{12} \text{ CNTs cm}^{-2}$. The number of walls in individual CNTs were eight for CNTs grown at both 0.13 and 1.3 Pa C_2H_2 (Fig. 6) and, thus, we conclude the number density of CNT walls to be $1.2 \times 10^{13} \text{ walls cm}^{-2}$. Fig. 7g schematically shows the CNT structure determined, in which the surface coverage of CNTs is as high as 58%. By using typical values for CNTs (7-nm diameter for the outermost wall, 0.35-nm radial interspacing between the walls, and $1.5 \times 10^{12} \text{ CNTs cm}^{-2}$ number density), we can calculate the mass density of the CNT array to be 1.25 g cm^{-3} , which is close to and, thus, consistent with the density determined by SEM-EDS. However, the number density of CNTs ($1.5 \times 10^{12} \text{ CNTs cm}^{-2}$) is about half that of the catalyst particles ($2.8 \times 10^{12} \text{ cm}^{-2}$, Fig. 2e) owing to the imperfect nucleation of CNTs and gradual deactivation of the catalyst particles during CVD. Therefore, there remains room for further enhancement of the CNT wall density beyond $2 \times 10^{13} \text{ cm}^{-2}$.

Fig. 7 – Cross-sectional SEM image of the CNT arrays on the growth substrate (a), and (b) bottom-view SEM and (c) AFM images of the same CNT arrays transferred to another Si substrate. The CNT arrays were grown at 400 °C from 0.40 Pa C₂H₂ for 7 min using the Ni/TiN catalyst under the same conditions as for Fig. 2e (400 °C, 8.1 pm s⁻¹, and -20 V bias voltage). (d,e) High-resolution AFM images of the CNT roots, corresponding to positions (d) and (e) shown in (c). (f) The same AFM image as Fig. 2e is shown at the same scale as (d,e) for comparison. (g) A schematic of the CNT structure in the array with the CNT number density of $1.5 \times 10^{12} \text{ cm}^{-2}$, an average CNT diameter of 7 nm, and number of CNT walls of eight.

We performed some characterization of quality and resistance of the CNTs. HRTEM images of individual CNTs were taken for the CNT arrays (Fig. S5). The dense (0.7 g cm^{-3})

array synthesized at 400 °C (Fig. S5a) was comprised of rather defective CNTs (Fig. S5b) whereas the less dense (0.3 g cm^{-3}) array synthesized at 500 °C (Fig. S5c) was comprised of less defective CNTs (Fig. S5d). These results show that the growth of individual CNTs gets much easier for a temperature increase by 100 °C. Current–voltage curves for various samples were obtained by AFM using a conductive tip with a curvature radius of $R = 25 \text{ nm}$. We obtained resistance values of 39–95 k Ω for CNTs grown at 400 °C, which are comparable with the previous works; 95 ± 46 , 35, 80 ± 60 k Ω for CNTs grown at 450, 475, 650 °C using AFM tips with $R = 20$, 20–30, $\sim 20 \text{ nm}$, respectively [21,32,33]. The resistance values should be affected by the contact resistance between the AFM tip and the CNT arrays, which could be reduced by forming appropriate contact layer [17]. How to improve the quality of CNTs at low CVD temperature as well as how to build a good electrical contact with CNT tips are remaining issues.

4. Conclusions

To realize the practical application of CNTs, requirements for both structure and process need to be satisfied. For via interconnects in LSIs, CNTs need to be prepared at high density ($\sim 10^{13}$ walls cm^{-2}) and at low temperature (≤ 400 °C) on a conductive underlayer. We propose a simple process for the preparation of dense catalyst particles through their nucleation and growth during conventional sputter deposition on device substrates but with carefully engineered conditions to control the moderate initial island density. We prepared moderately dense Ni islands on a conductive TiN layer by lowering the deposition rate to 8.1 pm s^{-1} , heating the substrate to 400 °C, and applying a -20 V bias voltage to the substrate. This led to a retained Ni particle density as high as $2.8 \times 10^{12} \text{ cm}^{-2}$ after annealing at 400 °C. We also proposed a simple process for CNT growth by conventional thermal CVD without using plasma but with carefully engineered conditions: low temperature of 400 °C with a low C_2H_2 pressure of $0.13\text{--}1.3 \text{ Pa}$ so as not to kill the catalyst.

From SEM-EDS analysis, we found that the 100- to 300-nm-tall CNT arrays had a mass density as high as $\sim 1 \text{ g cm}^{-3}$. We proposed and developed a new simple method to directly count the number of CNTs in the array, simply by transferring CNTs to a different substrate (TEM microgrids or Si substrates) with their roots up and by taking the plan-view HRTEM and bottom-view AFM images. Through these analyses, we found that Ni catalyst particles at $2.8 \times 10^{12} \text{ cm}^{-2}$ grew CNTs at $1.5 \times 10^{12} \text{ CNTs cm}^{-2}$ and $1.2 \times 10^{13} \text{ walls cm}^{-2}$. Such CNTs, formed on a conductive TiN layer at a maximum process temperature of just 400 °C using conventional sputtering and CVD apparatus, and showing electric conduction with few-tens-k Ω resistances to the TiN underlayer by AFM measurement, would be suitable for the practical application of CNTs to via interconnects in LSIs.

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References

- [1] Murakami Y, Chiashi S, Miyauchi Y, Hu M, Ogura M, Okubo T, et al. Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy. *Chem Phys Lett* 2004; 385(3–4):298–303.
- [2] Hata K, Futaba DN, Mizuno K, Nanami T, Yumura M, Iijima S. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* 2004;306(5700):1362–4.
- [3] Zhong G, Iwasaki T, Honda K, Furukawa Y, Ohdomari I, Kawarada H. Low temperature synthesis of extremely dense and vertically aligned single-walled carbon nanotubes. *Jpn J Appl Phys* 2005;44(4A):1558–61.
- [4] Noda S, Hasegawa K, Sugime H, Kakehi K, Zhang Z, Maruyama S, et al. Millimeter-thick single-walled carbon nanotube forests: hidden role of catalyst support. *Jpn J Appl Phys* 2007;46(17):L399–L401.
- [5] Awano Y, Sato S, Nihei M, Sakai T, Ohno Y, Mizutani T. Carbon nanotubes for VLSI: interconnect and transistor applications. *Proc IEEE* 2010;98(12):2015–31.
- [6] Robertson J, Zhong G, Esconjauregui CS, Bayer BC, Zhang C, Fouquet M, et al. Applications of carbon nanotubes grown by chemical vapor deposition. *Jpn J Appl Phys* 2012;51(1S):01AH01-1–8.
- [7] Yao Z, Kane CL, Dekker C. High-field electrical transport in single-wall carbon nanotubes. *Phys Rev Lett* 2000;84(13):2941–4.
- [8] McEuen PL, Fuhrer MS, Park HK. Single-walled carbon nanotube electronics. *IEEE Trans Nanotechnol* 2002;1(1):78–85.
- [9] Hamada N, Sawada S, Oshiyama A. New one-dimensional conductors: graphitic microtubules. *Phys Rev Lett* 1992;68(10):1579–82.
- [10] Miyata Y, Yanagi K, Maniwa Y, Kataura H. Optical evaluation of the

- metal-to-semiconductor ratio of single wall carbon nanotubes. *J Phys Chem C* 2008;112(34):13187–91.
- [11] Futaba DN, Hata K, Namai T, Yamada T, Mizuno K, Hayamizu Y, et al. 84% Catalyst activity of water-assisted growth of single walled carbon nanotube forest. *J Phys Chem B* 2006;110(15):8035–8.
- [12] Li H, Yin WY, Banerjee K, Mao JF. Circuit modeling and performance analysis of multi-walled carbon nanotube interconnects. *IEEE Trans Electron Devices* 2008;55(6):1328–37.
- [13] Sugime H, Noda S. Millimeter-tall single-walled carbon nanotube forests grown from ethanol. *Carbon* 2010;48(8):2203–11.
- [14] Amama PB, Pint CL, Kim SM, McJilton L, Eyink KG, Stach EA, et al. Influence of alumina type on the evolution and activity of alumina-supported Fe catalysts in single-walled carbon nanotube carpet growth. *ACS Nano* 2010;4(2):895–904.
- [15] Nihei M, Horibe M, Kawabata A, Awano Y. Simultaneous formation of multiwall carbon nanotubes and their end-bonded ohmic contacts to Ti electrodes for future ULSI interconnects. *Jpn J Appl Phys* 2004;43(4B):1856–9.
- [16] Sato S, Kawabata A, Kondo D, Nihei M, Awano Y. Carbon nanotube growth from titanium–cobalt bimetallic particles as a catalyst. *Chem Phys Lett* 2005;402(1–3):149–54.
- [17] Sato S, Kawabata A, Nozue T, Kondo D, Murakami T, Hyakushima T, et al. Fabrication of carbon nanotube via interconnects at low temperature and their robustness over a high density current. *Sens Mater* 2009;21(7):373–83.
- [18] Yamazaki Y, Saluma N, Katagiri M, Suzuki M, Sakai T, Sato S, et al. Synthesis of a closely packed carbon nanotube forest by a multi-step growth method using plasma-based chemical vapor deposition. *Appl Phys Exp* 2010;3(5):055002-1–3.

- [19] Esconjauregui S, Fouquet M, Bayer BC, Ducati C, Smajda R, Hofmann S, et al. Growth of ultrahigh density vertically aligned carbon nanotube forests for interconnects. *ACS Nano* 2010;4(12):7431–6.
- [20] Zhong GF, Warner JH, Fouquet M, Robertson AW, Chen BA, Robertson J. Growth of ultrahigh density single-walled carbon nanotube forests by improved catalyst design. *ACS Nano* 2012;6(4):2893–903.
- [21] Sugime H, Esconjauregui S, Yang J, D'Arsié L, Oliver RA, Bhardwaj S, et al. Low temperature growth of ultra-high mass density carbon nanotube forests on conductive supports. *Appl Phys Lett* 2013;103(7):073116-1–5.
- [22] Yamada K, Kaneko A, Kato H, Homma Y. Vertically-aligned carbon nanotube growth using closely packed iron oxide nanoparticles. *Mater Express* 2012;2(3):257–60.
- [23] Hu M, Noda S, Tsuji Y, Okubo T, Yamaguchi Y, Komiyama H. Effect of interfacial interactions on the initial growth of Cu on clean SiO₂ and 3-mercaptopropyltrimethoxysilane-modified SiO₂ substrates. *J Vac Sci Technol A* 2002;20(3):589–96.
- [24] Hu M, Noda S, Okubo T, Yamaguchi Y, Komiyama H. Structural and morphological control of nanosized Cu islands on SiO₂ using a Ti underlayer. *J Appl Phys* 2003;94(5):3492–7.
- [25] Amama PB, Pint CL, McJilton L, Kim SM, Stach EA, Murray PT, et al. Role of water in super growth of single-walled carbon nanotube carpets. *Nano Lett* 2009;9(1):44–50.
- [26] Hasegawa K, Noda S. Moderating carbon supply and suppressing Ostwald ripening of catalyst particles to produce 4.5-mm-tall single-walled carbon nanotube forests. *Carbon* 2011;49(13):4497–504.
- [27] Hultman L, Sundgren JE, Greene JE, Bergstrom DB, Petrov I. Highflux lowenergy (20 eV) N₂⁺ ion irradiation during TiN deposition by reactive magnetron sputtering: Effects

- on microstructure and preferred orientation. *J Appl Phys* 1995;78(9):5395–403.
- [28] Chen Z, Kim DY, Hasegawa K, Noda S. Methane-assisted chemical vapor deposition yielding millimeter-tall single-wall carbon nanotubes of smaller diameter. *ACS Nano* 2013;7(8):6719–28.
- [29] Hasegawa K, Noda S. Millimeter-tall single-walled carbon nanotubes rapidly grown with and without water. *ACS Nano* 2011;5(2):975–84.
- [30] Sugime H, Noda S. Cold-gas chemical vapor deposition to identify the key precursor for rapidly growing vertically-aligned single-wall and few-wall carbon nanotubes from pyrolyzed ethanol. *Carbon* 2012;50(8):2953–60.
- [31] Futaba DN, Hata K, Yamada T, Hiraoka T, Hayamizu Y, Kakudate Y, et al. Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nat Mater* 2006;5(12):987–94.
- [32] Nessim GD, Seita M, O'Brien KP, Hart AJ, Bonaparte RK, Mitchell RR, et al. Low temperature synthesis of vertically aligned carbon nanotubes with electrical contact to metallic substrates enabled by thermal decomposition of the carbon feedstock. *Nano Lett* 2009;9(10):3398–405.
- [33] Bayer BC, Zhang C, Blume R, Yan F, Fouquet M, Wirth CT, et al. In-situ study of growth of carbon nanotube forests on conductive CoSi_2 support. *J Appl Phys* 2011;109(11):114314-1–7.

Captions

Fig. 1 – Approaches for preparation of catalyst particle arrays on substrates. (a) Pre-forming catalyst particles and then depositing the particles on the substrate. (b) Pre-forming the catalyst layer on substrates and then transforming the layer into particles. (c) Directly nucleating and growing catalyst particles on substrates. (d,e) Our strategy for maintaining catalyst particles at high densities during CVD.

Fig. 2 – (a–e) AFM images of Ni particles deposited at different temperatures and deposition rates. The number densities of the Ni particles are shown in the images after annealing at 400 °C for 10 min. (f,g) The AFM images shown at a magnified height scale. (f) and (g) are of the same images as those as deposited (as sputtered) in (a) and (e), respectively. The scale bar for the lateral dimension in (a) applies for all images. And the scale bar for the height in (d) applies for the images (a–e).

Fig. 3 – Cross-sectional SEM images of CNTs grown by Ni catalyst on TiN at 400 °C from (a–d) 0.13 Pa and (e–h) 1.3 Pa C₂H₂ for (a,e) 5, (b,f) 10, (c,g) 30, and (d,h) 60 min.

Fig. 4 – (a) Height, (b) amount of carbon, and (c) mass density of the CNT arrays grown by Ni catalyst on TiN at 400 °C from 0.13 Pa (●) and 1.3 Pa (○) C₂H₂. The mass densities of the CNT arrays were initially 0.7–1.1 g cm⁻³ and decreased to ~0.75 g cm⁻³ after 30 min for both 0.13 and 1.3 Pa C₂H₂.

Fig. 5 – (a) Schematic of the transfer process of the CNT arrays from the growth substrates to TEM microgrids; the Ni/TiN/SiO₂ layer in between the Si substrate and the CNT array was etched by HF (25 wt%) solution, and the CNT arrays floating in the solution were captured by the microgrid. (b,c) Typical SEM images of the CNT array transferred to the TEM microgrid. (d–g) High-magnification, bottom-view SEM images of the CNT arrays

grown by Ni catalyst on TiN at 400 °C from (d,e) 0.13 and (f,g) 1.3 Pa C₂H₂ for (d,f) 5, (e) 25, and (g) 30 min. (h) The same AFM image of Ni catalyst particles as Fig. 2e is shown for comparison. The Ni particles were prepared under the same conditions as for Fig. 2e (400 °C and 8.1 pm s⁻¹ with -20 V bias voltage) and used to grow the CNTs in (d–g).

Fig. 6 – Cross-sectional SEM (a,c) and plan-view HRTEM (b,d) images of the CNT arrays grown at 400 °C from 0.13 (a,b) and 1.3 (c,d) Pa C₂H₂ using the Ni/TiN catalyst under the same conditions as in Fig. 2e (400 °C, 8.1 pm s⁻¹, and -20 V bias voltage). The CNT arrays were transferred to the TEM microgrids by the method shown in Fig. 5a.

Fig. 7 – Cross-sectional SEM image of the CNT arrays on the growth substrate (a), and (b) bottom-view SEM and (c) AFM images of the same CNT arrays transferred to another Si substrate. The CNT arrays were grown at 400 °C from 0.40 Pa C₂H₂ for 7 min using the Ni/TiN catalyst under the same conditions as for Fig. 2e (400 °C, 8.1 pm s⁻¹, and -20 V bias voltage). (d,e) High-resolution AFM images of the CNT roots, corresponding to positions (d) and (e) shown in (c). (f) The same AFM image as Fig. 2e is shown at the same scale as (d,e) for comparison. (g) A schematic of the CNT structure in the array with the CNT number density of $1.5 \times 10^{12} \text{ cm}^{-2}$, an average CNT diameter of 7 nm, and number of CNT walls of eight.