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High-yield, in-situ fabrication and integration of horizontal carbon nanotube arrays at the wafer scale for robust ammonia sensors

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ABSTRACT

This paper reports the successful experimental demonstration of the localized growth of horizontal, dense carbon nanotube (CNT) arrays in situ and at the wafer scale. The selectivity and directionality of the CNT catalytic growth process along with the adequate design and fabrication of the catalyst support enables the direct integration of nanotubes arrays into heterogeneous devices. This novel CNT integration method is developed to manufacture conductance based gas sensors for ammonia detection and is demonstrated to produce a yield above 90% at the wafer scale. Owing to its flexibility, the integration process can be useful for a wide range of applications and complies with industrial requirements in terms of manufacturability and yield, requirements for the acceptance of CNTs as alternate materials. A state-of-the-art CNT array resistivity of $1.75 \times 10^{-5}\ \Omega\,m$ has been found from the CNT characterization. When exposed to low NH_3 concentrations, the CNT sensors show good repeatability, long-term stability, and high design robustness and tackle the reproducibility challenge for CNT devices. Individual device calibration is not needed. The ammonia adsorption isotherm on the sensor is well fitted by Freundlich equation. The extrapolated detection limit is about 1 ppm. The dependence of the sensitivity with temperature indicates that ammonia sensing is likely to involve an endothermic process. Finally, relative humidity cross sensitivity has been found to have no adverse effect on the ammonia response enabling NH_3 monitoring in ambient conditions.

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Abbreviations: CNT, carbon nanotube; CVD, chemical vapor deposition; DC, direct current; FET, field effect transistor; *I–V*, current–voltage; MWCNT, multi-walled carbon nanotube; NEMS, nano-electro-mechanical systems; RF, radiofrequency; RH, relative humidity; SEM, scanning electron microscopy; SWCNT, single-walled carbon nanotube; TEM, transmission electron microscopy; TLV, threshold limit value; UV, ultraviolet.

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1. Introduction

The publication in the early 90's by Iijima about helical microtubules of graphitic carbon [1], now more familiar as carbon nanotubes (CNT), has generated since, intense research on this carbon nanomaterial. Findings about their unique mechanical and electrical properties has further fueled the interest on CNTs [2,3]. Carbon nanotubes exhibit high Young's modulus with low volumetric mass density and good electrical conductivity without electromigration issues [4]. As a logical outcome, CNTs have been integrated in a broad spectrum of applications: field-effect transistor (FET) based logic gates [5], interconnect lines [6–8], micro- and nano-electro-mechanical systems (MEMS and NEMS)[9,10] or chemical sensors [11]. In particular, Kong's et al. paper [12] in 2000 reported the first CNT gas sensor: a semiconducting single wall carbon nanotube (SWCNT) FET that showed opposite resistance shifts upon exposure to NO_2 and NH_3, and aroused the interest in CNTs as a promising candidate for a building block for ambient gas sensors.

As a result of their dimensions and structure, carbon nanotubes are ideal primary transducers. Since they are a hollow material with a high surface-to-volume ratio, when a molecule adsorbs on the nanotube the change on its surface produces a signal with a high signal-to-noise ratio [13]. The integration of high density CNT arrays in sensor structures provides a large detection and transduction surface, potentially leading to an improved sensitivity. Finally, the susceptibility and electronic structure of carbon nanotubes promote sensor response to ultra-low concentrations of gas molecules with detection limits in the range of ppm or ppb for various gases as reported in literature [14].

Despite being a promising material with potential to produce innovative devices for a wide range of fields, no commercial application of CNT based sensors or electronic applications for CNTs in general has made its way out of the lab and into the market. The approval of CNTs as an alternative material in industry has been impeded by major integration obstacles [15] at the wafer scale (such as the large production of CNTs at the right place and with suitable orientation). Also, CNT gas sensing has been hindered by robustness issues such as response variability from device to device or the failure FET sensors using single nanotubes. This work presents a novel method of CNT integration that addresses some of the most important impediments to the implementation of carbon nanotubes as an alternate material for commercial applications. Namely, this research presents an experimental demonstration of the fabrication of localized, horizontally, in-situ grown, dense carbon nanotube (CNT) arrays at the wafer scale. Direct integration of nanotube arrays into devices is enabled by combining the selectivity and directionality of an optimized CNT catalytic chemical vapor deposition (CVD) growth process with the adequate design and fabrication of a catalyst support. This novel, high throughput CNT integration method is developed and evidenced by the manufacture of conductance based gas sensors based on CNT arrays for ammonia detection. The interest concerning ammonia detection comes from the wide use of this chemical compound in human activities (mainly agriculture) and its adverse effects on human health (by causing notably respiratory illnesses), on the environment, freshwaters and soils. Ammonia's toxicity to aquatic life and its contribution to acid rains are reasons to classify this gas as a chemical environmental hazard. The threshold limit values (TLV) which are the safety exposure limits below which human health is deemed not to be at risk, have been defined as 35 ppm for short term exposure (15 min), a time weighted concentration of 25 ppm over ten hours per day, and 300 ppm as the concentration immediately dangerous to life and health [16]. With the objective of developing a sensor capable of being used in ambient conditions, the CNT material characteristics have first been studied and the CNT-based sensor robustness, reliability and sensing capabilities towards ammonia have been assessed taking into account the influence of temperature and humidity.

2. Wafer-scale CNT integration

The wafer-scale growth of multiple CNT arrays is achieved by activating a "carpet growth mode" via a catalytic chemical vapor deposition (CVD) process previously developed [17,18]. In order to integrate in-situ horizontal CNT arrays directly into the gas sensor structure, the selective and directional CVD growth process is only activated from the vertical sidewall of a thoughtfully designed, line-shape patterned catalyst support.

2.1. *Catalyst support*

The main steps of the fabrication process for the integration of CNTs into gas sensing devices are schematically illustrated in Fig. 1. All fabrication steps are compatible with full wafer processing, which should allow high throughput, and are performed here on 4" wafers. Catalyst support fabrication begins by sputtering a stack of layers: TiN, Al_2O_3, and TiN again followed by SiO_2 (Fig. 1a), on a p-doped Si/SiO_2 wafer. The nitride-oxide-nitride alternating stack is designed to achieve a selective growth of CNTs. The SiO_2 top layer is patterned and used as a hard mask (Fig. 1b). A dry etch process is used to pattern the TiN/Al_2O_3 layers to create catalyst support lines (Fig. 1c) with a vertical profile needed to grow CNTs horizontally. The stop-etch at the bottom TiN layer and catalyst support slope constancy are critical features for the successful activation and growth of horizontal CNT arrays from the catalyst support line sidewall. The device electrodes are also patterned by dry-etching the bottom TiN layer (Fig. 1d). Post-etch cleaning is necessary to remove etching by-products and other residues in order to get clean and smooth nucleation surfaces propitious to CNT growth. Fe catalyst with a targeted thickness of 1 nm is then evaporated and locally deposited with a 45° tilt angle on a single sidewall of the electrodes by means of a photo-resist mask patterned by standard UV-lithography and lift-off (Fig. 1e).

2.2. *CVD growth process*

Heating, annealing the thin catalyst layer leads to the formation of Fe nanoparticles that act as seeds for the CNTs in the