We introduce a novel nanofabrication technique to directly deposit catalyst pads for the chemical vapor deposition synthesis of single-walled carbon nanotubes (SWCNTs) at any desired position on a substrate by focused ion beam (FIB) induced deposition of silicon oxide thin films from the metalorganic precursor tetraethyl orthosilicate (TEOS). A high resolution in the positioning of the SWCNTs is naturally achieved as the imaging and deposition by the FIB are conducted concurrently in situ at the same selected point on the substrate. This technique has substantial advantages over the current state-of-the-art methods that are based on complex and multistep lithography processes.

In this work, the synthesized SWCNTs are characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and Raman spectroscopy. The composition and morphology of the catalyst thin films are investigated by energy-dispersive X-ray spectroscopy (EDS) and AFM, respectively. The yield of the synthesized SWCNTs is studied as a function of the dimensions of the deposited thin-film pads, and the optimum values for only one SWCNT on average to be grown from a thin-film pad are found.

Figure 1 shows a schematic diagram of the nanofabrication process. First, in a commercial FIB system (SII NanoTechnology SM9800SE), a gallium FIB is used to decompose TEOS molecules at specific locations on a silicon oxide substrate, which induces the deposition of silicon oxide thin film pads at these locations. The FIB-induced deposition is conducted with a gallium ion beam energy of 30 keV at a pressure of $3 \times 10^{-3}$ Pa. The areas of the deposited thin film pads used in this study are $2 \times 2$, $5 \times 5$, and $5 \times 10$ µm², with thicknesses ranging from 3 to 700 nm. After the film deposition, carbon nanotubes are synthesized by thermal CVD in a quartz tube furnace (Asahi Rika). The CVD recipe is as follows. The furnace is preheated to 900°C in air. The substrate is inserted directly from room temperature into the furnace and annealed in a flow of O₂ (100 sccm) and Ar (400 sccm) mixture for 30 min at 900°C. Next, the furnace is evacuated down to a pressure of 1 Pa and then Ar is injected inside the furnace until the pressure reaches 1 atm, followed by a flow of H₂ (200 sccm) for 1 min. Finally, the carbon nanotubes from the thin-film pads are synthesized under the coflow of CH₄ (300 sccm) and H₂ (200 sccm) for 20 min. After the synthesis, the furnace is cooled to room temperature in H₂ flow.

Figure 2 presents SEM images of the synthesized carbon nanotubes (Hitachi SU-70). From a film pad deposited over an area of $5 \times 10$ µm² and a thickness of 10 nm, tens of
carbon nanotubes are grown, with lengths up to several microns [Fig. 2(a)]. On the other hand, only one and long (several tens of microns) carbon nanotube is obtained from a 2 × 2µm² pad, with the same thickness of 10 nm [Fig. 2(b)].

To elucidate the nature of the synthesized carbon nanotubes, AFM (Hitachi Nanocute), and Raman spectroscopy (Renishaw InVia) are used. An AFM topography image of a typical synthesized carbon nanotube is shown in Fig. 3(a). From its height profile [Fig. 3(b)], the estimated diameter of the nanotube is about 1.7 nm. The Raman spectroscopy measurement of a synthesized SWCNT is shown in Figs. 3(c) and 3(d). The G-band peak (detected with a 532-nm-wavelength laser) appears as expected at around 1580 cm⁻¹, and there is no apparent D-band peak, which indicates that the synthesized SWCNT is nearly defect-free. The RBM peak is detected (with a 633-nm-wavelength laser) at the frequency \( \omega_{\text{RBM}} = 194 \text{ cm}^{-1} \) that corresponds to a SWCNT diameter of \( d = 1.3 \text{ nm} \) according to the formula \( d = 248/\omega_{\text{RBM}} (\text{nm}) \).

Furthermore, to define the chirality of this SWCNT, a Kataura plot analysis is performed, as shown in Fig. 3(e). The laser energy of 1.96 eV (633 nm wavelength) should be in resonance (with a typical resonance window of 50 meV) with one of the optical transitions of the SWCNT, which, in this case, corresponds to the metallic SWCNT, with the chirality (12,6) and diameter of 1.26 nm. This is indeed in excellent agreement with the calculated value of 1.3 nm from the RBM frequency. All the synthesized SWCNTs in this work have typical diameters between 1 and 3 nm.

It is widely accepted, and confirmed both experimentally and theoretically, that the main mechanism of the synthesis of carbon nanotubes by CVD is the so-called vapor–liquid–solid (VLS) mechanism, in which catalyst nanoparticles act as “seeds” for the growth of carbon nanotubes. Figure 4(a) shows an AFM topography image of a SWCNT emerging from a cluster of nanoparticles originating from a deposited film of 10 nm thickness. The diameter of the nanoparticles is comparable to that of the synthesized SWCNTs [Fig. 4(b)], which proves that they can act as catalysts for the synthesis of the SWCNTs via the VLS mechanism. However, the most common catalyst nanoparticles used for the synthesis of carbon nanotubes by CVD are made of the transition metals Fe, Co, and Ni, which are absent in this current work. To explore the material composition of the catalyst nanoparticles obtained in our experiments, an EDS analysis (EDAX/AMETEK Genesis APEX4) in the SEM facility is performed. Figure 4(c) shows EDS spectra, obtained with an electron beam energy of 5 keV, of a 10-nm-thick film after FIB deposition and of the resulting nanoparticles from the same film after CVD. After the FIB deposition, in addition to Si and O, the film contains significant amounts of gallium and carbon. Clearly, Ga originates from the FIB and carbon from the TEOS precursor or/and carbon contamination in the FIB system chamber. However, after CVD, Ga and C peaks are absent, and only Si and O peaks remain. This is explained by the fact that, during the CVD process, carbon is burned away by oxygen annealing, and gallium is evaporated at the high operating temperature (900 °C). Furthermore, it is found that, if the CVD recipe does not include annealing in O₂, carbon nanotubes are not synthesized (see the online supplementary data at http://stacks.iop.org/APEX/11/085101/mmedia).

Hence, the removal of carbon by annealing before the synthesis is crucial.

From the above analysis results, it is concluded that the catalyst nanoparticles in our work are made of silicon oxide or of the general nonstoichiometric form SiOₓ. Indeed, several previous reports have shown that SiOₓ nanoparticles can be used as catalysts for the synthesis of SWCNTs by CVD. Moreover, it has recently been reported by Zhang et al. that SWCNTs could be selectively grown with metallic or semiconducting properties by tuning the size of
the catalyst SiO$_x$ nanoparticles and the CVD recipe. It is noted that our CVD recipe is similar to a recipe reported in Ref. 22. However, in contrast to their results, we could not obtain SWCNTs without O$_2$ annealing. This could be explained by the expected low content of carbon in their SiO$_x$ films, which were made by sputtering, in contrast to our FIB-deposited films.

Different FIB-deposited thin-film dimensions and CVD recipes were tried in order to optimize the control of the yield of the synthesized SWCNTs (see the online supplementary data at http://stacks.iop.org/APEX/11/085101/mmedia). Specifically, to obtain just one SWCNT on average, the optimum initial film dimensions should be around $2 \times 2 \mu m^2$ and 10 nm in area and thickness, respectively. If either the area or thickness is increased, the yield (i.e., the number) of synthesized SWCNTs increases. Any area or thickness smaller than the optimized values generally does not yield any carbon nanotubes (see the online supplementary data at http://stacks.iop.org/APEX/11/085101/mmedia).

For applications, our suggested nanofabrication technique will be very useful when the precise positioning of a SWCNT at or near a specific point on a substrate is required.
example, in the synthesis of a SWCNT directly on metal electrodes for electrical transport characterization\(^{2,23-25}\) and in the positioning of a SWCNT over a nanopore for biological molecule sensing.\(^{26}\) On the other hand, if a high resolution in the positioning of individual SWCNTs is not required and/or a large area on a substrate must be patterned by SWCNTs, then conventional lithography techniques would be more effective in terms of processing time and cost. Furthermore, for nanodevice applications, our method can be dramatically improved by simultaneously controlling the alignment of the synthesized SWCNTs by either substrate-oriented growth\(^{25,27,28}\) or gas-flow-rate control during CVD.\(^{29,30}\)

Another interesting idea is to explore different precursors for the FIB-induced deposition that might lead to more efficient catalyst nanoparticles for the CVD synthesis of carbon nanotubes.

In summary, we introduced a novel nanofabrication technique for controlling the position of single-walled carbon nanotubes on a substrate, without the use of lithography methods. It consists of the deposition of silicon oxide nanoparticles thin films using a gallium focused ion beam at desired points on a substrate, with the nanoparticles acting as catalysts for the CVD synthesis of single-walled carbon nanotubes at these specific points. The optimum area and thickness of the thin-film catalyst required for the synthesis of only one nanotube on average was determined. The proposed technique is an important contribution to the field of carbon nanotube synthesis and nanofabrication.

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