

## Few graphene layers/carbon nanotube composites grown at complementary-metal-oxide-semiconductor compatible temperature

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We investigate the growth of the recently demonstrated composite material composed of vertically aligned carbon nanotubes capped by few graphene layers. We show that the carbon nanotubes grow epitaxially under the few graphene layers. By using a catalyst and gaseous carbon precursor different from those used originally we establish that such unconventional growth mode is not specific to a precise choice of catalyst–precursor couple. Furthermore, the composite can be grown using catalyst and temperatures compatible with complementary-metal-oxide-semiconductor processing ( $T < 450$  °C). © 2011 American Institute of Physics. [doi:10.1063/1.3569142]

The limitations of copper interconnects are driving research toward alternative materials and technologies for the next-generation of integrated circuits (ICs). Carbon nanomaterials, with their many attractive properties, are emerging as front-runners to potentially replace copper for interconnects and passive devices in ICs, including vias, through-silicon vias and horizontal wires.<sup>1–4</sup> Indeed, low-dimensional allotropes of carbon [in particular, carbon nanotubes (CNTs) and graphene] have extraordinary physical properties because of their unique structure. Contrary to copper, CNTs can accept a high current density and can have an extremely high thermal conductivity.<sup>5,6</sup> Graphene has the potential for ultrahigh electrical conductivity.<sup>7</sup> Beside these advantages for interconnects technology, Field effect transistors have been demonstrated on CNTs and graphene.<sup>8,9</sup> It could be very interesting to combine these advances in interconnects and transistor technologies in an all carbon electronics. Recent theoretical works have confirmed the interest of devices that may use combinations of graphene layers and CNTs for nanoelectronics applications.<sup>10</sup> Varshney *et al.* have shown that, in principle, the “pillared-graphene” architecture could be also an attractive candidate to quickly dissipate thermal energy in integrated devices.<sup>11</sup> Dimitrakakis *et al.*<sup>12</sup> have investigated this architecture from the perspective of hydrogen storage. However, the success of these approaches strongly depends on the ability to assemble CNTs and graphene in working devices.

Recently, Fujitsu Corp. has demonstrated the possibility of building carbon interconnect structures combining CNTs and few graphene layers (FGLs) (Ref. 13) (these structures will be referred to as “composite” in the following). This approach of binding CNTs and FGLs during the growth itself may be a powerful method to produce CNT/graphene hybrid systems.

Here, we show that such composite is composed of CNTs epitaxially grown below the FGLs. We show that the composite can be obtained independently of the choice of the precursor and catalyst indicating that this unusual growth mode is in fact quite general. Furthermore, we achieved growth using catalyst and temperatures compatible with back

end of line (BEOL) processing. This opens new possibilities concerning its integration in next generations of interconnects.

Figure 1 shows scanning electron microscope (SEM) images of the product of chemical vapor deposition (CVD) on 6 nm thick nickel films. The growth was performed at 550 °C in an Applied Material 200 mm DXZ chamber using propylene ( $C_3H_6$ ) as carbon source. Nickel films were deposited by physical vapor deposition on a 10 nm TiN layer deposited by CVD on a standard silicon 200 mm wafer. Depending on the pretreatment (initial step before the introduction of propylene) very different results are obtained. On one hand, with

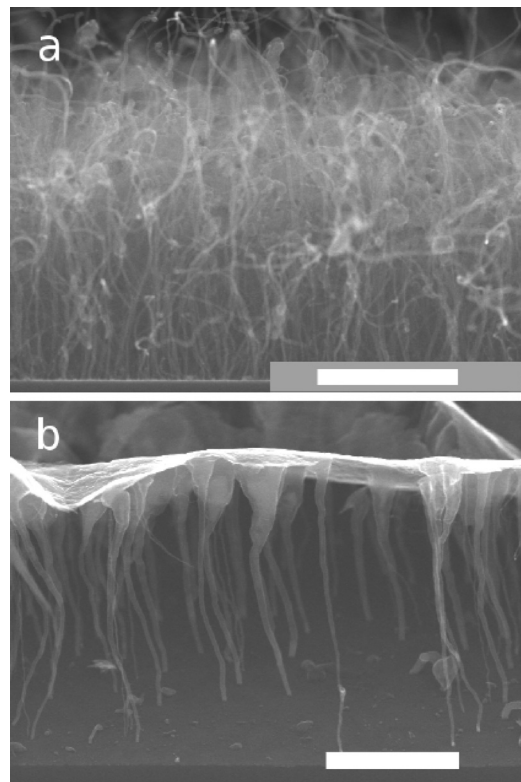


FIG. 1. Result of the CVD growth at 550 °C during 30 min. (a) Prior to growth, argon was flown at 30 Torr during 30 min. Propylene was then introduced at 30 Torr. (b) Propylene was introduced in the chamber without argon pretreatment. The scale bar is 1  $\mu$ m in both images.

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a pretreatment consisting of an argon flow during 15 min, CNTs are obtained [Fig. 1(a)]. The nanotubes are multiwall with catalyst at the tip and about 10 nm in diameter (not shown). On the other hand, in absence of pretreatment a complex nanostructure composed of a forest of nanotubes with a thin layer bonded on top of it is formed [Fig. 1(b)].

A similar nanostructure was observed by Kondo and colleagues by CVD at 510 °C using cobalt as catalyst and acetylene ( $C_2H_2$ ) as carbon precursor.<sup>13</sup> They proposed the following mechanism for the growth of this composite. When a substrate with a catalyst film is heated in presence of carbon precursor, the catalytic film first decomposes the source gas while remaining in its thin-film structure. This leads to the formation of graphene multilayer on the catalyst. Second, the catalyst film breaks into particles. Third, multi-wall CNTs are synthesized from catalyst particles by the tip growth mode.

Multi- and single-layer graphene are well known to form on nickel films.<sup>14–18</sup> CNTs are also well known to grow from nickel nanoparticles.<sup>19–21</sup> It is therefore surprising that the composite has not yet been reported on Ni. This fact, together with our observations already indirectly confirms the scenario proposed by Kondo and colleagues.<sup>13</sup> Indeed, in the CNT community, very thin Ni layers (1 nm or less) are dewetted into small droplets that subsequently catalyze the nanotube growth. The thinner the film the smaller the particles and therefore the thinner the nanotubes. This is important because the goal here is to synthesize the thinnest nanotubes which are more likely to show interesting effects such as quantum confinement.<sup>22</sup> On the contrary, in the graphene community relatively large Ni thicknesses (typically larger than 100 nm) are used since one wants to avoid a discontinuous graphene layer due to dewetting. We used a catalyst layer of intermediate thickness (few nanometer) which may represent a better compromise between the necessity to keep the catalyst film intact during FGLs growth and the necessary dewetting after some time to start nanotube growth. This is confirmed by the observation that when the nickel film is intentionally dewetted using argon pretreatment only nanotubes are formed. This is also confirmed by the SEM images taken at the initial stages of the composite growth. After 5 min of growth under the same conditions as in Fig. 1(b) there is an extended carbon film at the surface of the sample. In some places the catalyst has already dewetted and the CNTs growth has started. This is evidenced by bumps at the surface under which it is possible to see nanotubes below the film (see Fig. 2). Therefore our observation clearly establishes that the FGLs film is formed first.

Figure 3 presents SEM and high resolution transmission microscope (HRTEM) images of the junction between a nanotube and the FGLs. The composite has been collected on an amorphous carbon TEM grid for HRTEM investigations. The nanotube are epitaxial under less than ten layers of graphene. In the previous study,<sup>13</sup> there were indications that the nanotube originated from holes in the first graphene layer forming a trumpet-like structure [Fig. 3(c)]. Figure 3(a) clearly illustrates that in our case a closed nanotube is in fact epitaxially formed under the FGL [sketched in Fig. 3(d)]. The shape of this interface may therefore depend on the experimental conditions. This will have to be deeply investigated since it can have important consequences concerning electrical contact between the nanotube and the FGL. Indeed,

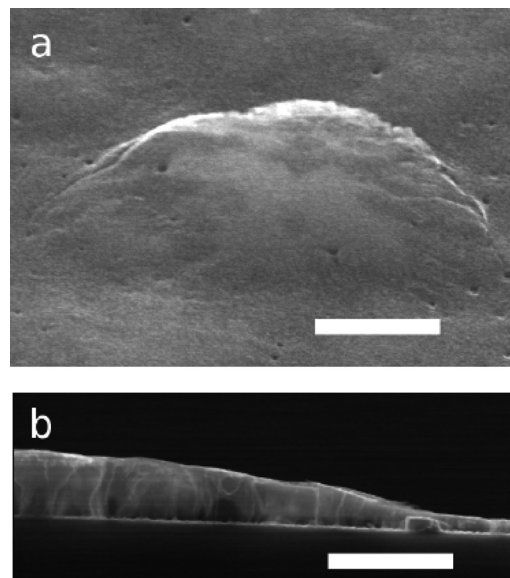


FIG. 2. Initial stage of the composite growth. The images are taken after growth in the same condition as in Fig. 1(b) but the growth lasted 5 min instead of 30 min. (a) Top view of the sample showing a bump in the FGLs film below which CNT growth has started. The scale bar is 200 nm. (b) Side view of a larger bump illustrating the presence of nanotubes. The scale bar is 400 nm.

the contact resistance can be expected to be larger in our case than in a configuration where the nanotube gradually transforms into a flat graphene sheet. Still, the contact electrical resistance should be reasonable given that the graphene orientation in the nanotube and the FGL should match due to their epitaxial relation.<sup>23</sup> This will have to be studied by electrical measurements. The fact that the nanotube is closed by

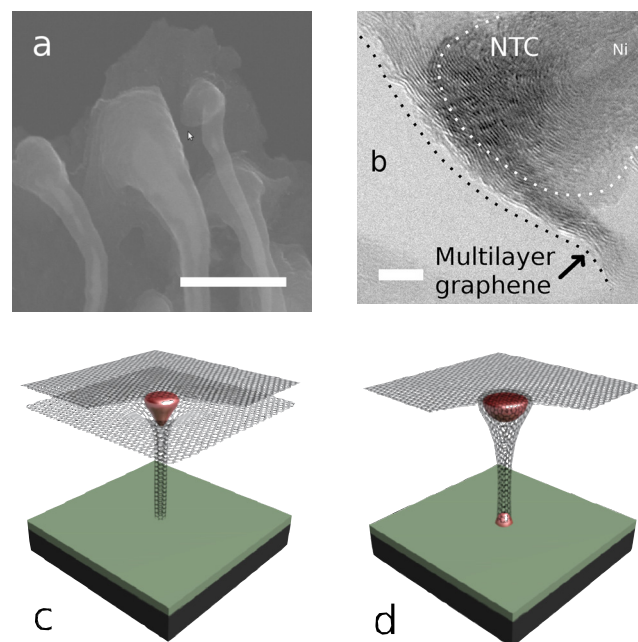


FIG. 3. (Color online) (a) Connection between nanotubes and FGLs viewed from below by SEM. Ni catalyst can be seen in the CNTs. The scale bar is 300 nm. (b) HRTEM image of the CNT/FGL interface. The dotted lines are guides for the eyes to localize the nanotube tip and the FGLs sheet. The scale bar is 5 nm. [(c) and (d)] Sketch of the two possible arrangements for the CNT/FLG interface. Our results indicate that the interface corresponds to the configuration depicted in (d) and that the nanotubes grow from a catalyst particle located at their root.

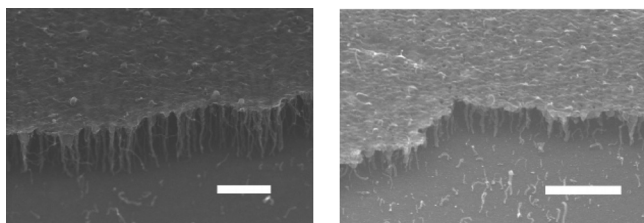


FIG. 4. Impact of the deposition temperature on the composite growth. (a) Growth at 450 °C. (b) Growth at 400 °C. In both cases a 15 min pretreatment with argon was made prior the growth under 15 Torr of  $C_3H_6$  during 15 min. The scale bar is 600 nm for both images.

a relatively important number of graphene layers suggests that CNTs grow from the root and not from their tip. Indeed, growth stops whenever the catalyst is completely encapsulated.<sup>20</sup> The reduction in their diameter toward the substrate can be attributed to the loss of catalyst material during the catalyst elongation/contraction process occurring during CNT growth.<sup>20</sup>

Some issues concerning this mechanism remain unclear. In particular, why does the catalyst film breaks into particles after some time? In the context of CNTs, nickel atoms exhibit fast self-diffusivity in presence of graphene interface.<sup>20,21</sup> At the initial stage of CNT formation, graphene layers grow at the catalyst step edges and catalyst atoms rapidly move toward the graphene-free region. This causes an elongation of the catalyst until the energy gained when binding graphene to the Ni surface no longer compensate the increase in the Ni surface energy. At this moment, the catalyst collapses into a more or less round particle.<sup>20</sup> We believe an analogous rapid diffusion of nickel atoms occurs in our case leading to the formation of catalyst particles, although we do not have direct evidences. Another key question concerns the way the carbon precursor is provided to the catalyst after the graphitic film is formed. Indeed, graphene is a good barrier to gas diffusion<sup>24</sup> and nanotube CVD growth stops when the catalyst particle is encapsulated.<sup>20</sup> These questions will have to be investigated by *in situ* measurements to fully determine the detailed growth process.

We have also investigated the possibility to grow such type of composite at lower temperatures. This point is critical in the case of the cointegration of these carbon structures with complementary-metal-oxide-semiconductor architecture at the interconnection levels since the maximum temperature acceptable during the device fabrication is 450 °C. As can be seen on Fig. 4, composites are also obtained at temperatures as low as 400 °C. Note that at these temperatures, dewetting does not occur as easily as at 550 °C and the initial pretreatment with argon is necessary to achieve the composite. This is not surprising since Ni self-diffusion should be slower at lower temperatures. As expected, the lower the temperature, the shorter the CNTs. It appears that the quality of the multilayer graphene film degrades with decreasing temperature as seen from the number of visible defects on the SEM pictures.

In conclusion, we have been able to synthesize epitaxial CNT/FGLs interface using a set of catalyst and precursor different from those used in Ref. 13. It establishes that this mechanism is quite general and that it can be expected to occur in a broader range of conditions than initially presented. Furthermore, the synthesis is fully compatible with interconnect technology since we used nickel catalyst (which is allowed at BEOL levels) and low temperatures. We believe that carefully adjusting the catalyst layer thickness, temperature, and other parameters one may be able to achieve single layer graphene on CNTs.

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- <sup>1</sup>F. Kreupl, A. P. Graham, G. S. Duesberg, W. Steinhögl, M. Liebau, E. Unger, and W. Hönlein, *Microelectron. Eng.* **64**, 399 (2002).
- <sup>2</sup>M. Nihei, D. Kondo, A. Kawabata, S. Sato, H. Shioya, M. Sakae, T. Iwai, M. Ohfuti, and Y. Awano, Proceedings of IEEE International Interconnect Technology Conference, 2005, pp. 234–236.
- <sup>3</sup>Y. Awano, *IEICE Trans. Electron.* **E89-C**, 1499 (2006).
- <sup>4</sup>T. Wang, K. Jeppson, N. Olofsson, E. E. B. Campbell, and J. Liu, *Nanotechnology* **20**, 485203 (2009).
- <sup>5</sup>Z. Yao, C. L. Kane, and C. Dekker, *Phys. Rev. Lett.* **84**, 2941 (2000).
- <sup>6</sup>P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, *Phys. Rev. Lett.* **87**, 215502 (2001).
- <sup>7</sup>P. Neugebauer, M. Orlita, C. Faugeras, A.-L. Barra, and M. Potemski, *Phys. Rev. Lett.* **103**, 136403 (2009).
- <sup>8</sup>S. J. Tans, A. R. M. Verschueren, and C. Dekker, *Nature (London)* **393**, 49 (1998).
- <sup>9</sup>Y. M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and Ph. Avouris, *Science* **327**, 662 (2010).
- <sup>10</sup>F. D. Novaes, R. Rurali, and P. Ordejon, *ACS Nano* **4**, 7596 (2010).
- <sup>11</sup>V. Varshney, S. S. Patnaik, A. K. Roy, G. Froudakis, and B. L. Farmer, *ACS Nano* **4**, 1153 (2010).
- <sup>12</sup>G. K. Dimitrakakis, E. Tyliaakis, and G. E. Froudakis, *Nano Lett.* **8**, 3166 (2008).
- <sup>13</sup>D. Kondo, S. Sato, and Y. Awano, *Appl. Phys. Express* **1**, 074003 (2008).
- <sup>14</sup>Y. Gamo, A. Nagashima, M. Wakabayashi, M. Terai, and C. Oshima, *Surf. Sci.* **374**, 61 (1997).
- <sup>15</sup>Q. Yu, J. Lian, S. Siriponglert, H. Li, Y. P. Chen, and S.-S. Pei, *Appl. Phys. Lett.* **93**, 113103 (2008).
- <sup>16</sup>A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, *Nano Lett.* **9**, 30 (2009).
- <sup>17</sup>A. J. Pollard, R. R. Nair, S. N. Sabki, C. R. Staddon, L. M. A. Perdigo, C. H. Hsu, J. M. Garfitt, S. Gangopadhyay, H. F. Gleeson, A. K. Geim, and P. H. Beton, *J. Phys. Chem. C* **113**, 16565 (2009).
- <sup>18</sup>K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Hong, *Nature (London)* **457**, 706 (2009).
- <sup>19</sup>Z. F. Ren, Z. P. Huang, D. Z. Wang, and J. G. Wen, *Appl. Phys. Lett.* **75**, 1086 (1999).
- <sup>20</sup>S. Helveg, C. López-Cartes, J. Sehested, P. L. Hansen, B. S. Clausen, J. R. Rostrup-Nielsen, F. Abild-Pedersen, and J. K. Nørskov, *Nature (London)* **427**, 426 (2004).
- <sup>21</sup>S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, A. C. Ferrari, R. Dunin-Borkowski, S. Lizzit, L. Petaccia, A. Goldoni, and J. Robertson, *Nano Lett.* **7**, 602 (2007).
- <sup>22</sup>S. Frank, P. Poncharal, Z. L. Wang, and W. A. De Heer, *Science* **280**, 1744 (1998).
- <sup>23</sup>S. Paulson, A. Helser, M. B. Nardelli, R. M. Taylor, M. Falvo, R. Superfine, and S. Washburn, *Science* **290**, 1742 (2000).
- <sup>24</sup>J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. Van der Zande, J. M. Parpia, H. G. Craighead, and P. L. McEuen, *Nano Lett.* **8**, 2458 (2008).