coatings

MDPI

Article

The Advantages of Double Catalytic Layers for Carbon Nanotube Growth at Low Temperatures (<400 °C) in 3D Stacking and Power Applications

Hong-Yi Lin [1], Nilabh Basu [2], Min-Hung Lee [3], Sheng-Chi Chen [4,5] and Ming-Han Liao [1,2,*]

[1] Department of Mechanical Engineering, National Taiwan University, Taipei 10617, Taiwan
[2] Graduate School of Advanced Technology, National Taiwan University, Taipei 10617, Taiwan
[3] Graduate Institute of Electro-Optical Science and Technology, National Taiwan Normal University, Taipei 10617, Taiwan
[4] Department of Materials Engineering and Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taipei 243303, Taiwan
[5] Taiwan and College of Engineering, Chang Gung University, Taoyuan 33302, Taiwan
[*] Correspondence: mhliaoa@ntu.edu.tw; Tel.: +886-918-936-625; Fax: +886-227-282-100

Abstract: A double catalytic layer scheme is proposed and investigated for the low temperature growth of carbon nanotubes (CNTs) over Co (Cobalt), Al (Aluminum), and Ti (Titanium) catalysts on a silicon substrate. In this work, we demonstrate the growth of CNTs by a thermal chemical vapor deposition (TCVD) process at both 350 °C and 400 °C. Based on scanning electron microscopy (SEM) and Raman spectroscopy analyses, the good quality of the CNTs is demonstrated. This study contributes to the on-going research on integrating semiconductors into packaging and power-related applications, as demonstrated with the low resistance (~128 Ω) and high thermal conductivity (~29.8 Wm^{-1} K^{-1}) of our developed CNTs.

Keywords: carbon nanotubes; low temperature; thermal conductivity; package

check for updates

Citation: Lin, H.-Y.; Basu, N.; Lee, M.-H.; Chen, S.-C.; Liao, M.-H. The Advantages of Double Catalytic Layers for Carbon Nanotube Growth at Low Temperatures (<400 °C) in 3D Stacking and Power Applications. *Coatings* **2023**, *13*, 965. https://doi.org/10.3390/coatings13050965

Academic Editor: Luca Valentini

Received: 25 April 2023
Revised: 16 May 2023
Accepted: 19 May 2023
Published: 22 May 2023

1. Introduction

Carbon nanotubes (CNTs) exhibit excellent mechanical properties, thermal conductivity (k), and electrical conductivity [1,2], making them a promising material for many applications [3]. In our previous work [4], we grew high quality CNTs using the thermal chemical vapor deposition (T-CVD) method with ferrocene as a catalyst at ~550 °C, resulting in a through-silicon via (TSV) structure. The electrical properties and high k of CNTs render them viable for utilization in three-dimensional integrated circuits (3DICs). However, for CNTs to be utilized in advanced packaging technology, it is imperative to maintain their excellent performance while reducing the growth temperature to below 400 °C. We proposed using an Al catalytic metal layer film as a barrier layer to successfully grow CNTs at 350 °C, and reported the results on material quality and the k value in our previous work [5]. In this work, we further utilize a Co catalytic layer for the growth of CNTs due to its lower temperature requirement for reduction compared to Fe [6]. Moreover, Co possesses properties similar to Fe and Ni metals [7]. To further enhance the catalytic efficiency, we introduce an Al catalytic layer as a barrier to prevent sintering of the catalytic particles. Additionally, we also include a Ti catalytic layer as an adhesion layer to minimize the energy loss resulting from interactions; as a result, we establish metal catalytic layers consisting of Co/Al/Co/Ti. In [8], the authors mentioned that in order to prevent spontaneous cap formation, a strong binding strength is required. Co possesses a higher binding strength, making it more suitable as a catalyst layer material for low-temperature growth of carbon nanotubes. In [9], when a Co-Al catalytic layer was compared with pure Fe and pure Ni metal layers, it exhibited a higher growth rate and surface quality. In another work [10], H. Sugime et al. used a similar combination of Co/Al/Mo/Cu metal multilayers as the catalyst for the growth of CNTs, but in their work, the reported Raman spectra values of peak (I_D/I_G) intensity, indicating the defect level, were high compared to this work. In addition, Y. Xiao et al. [11] and S. Li et al. [12] used a Ni/Al/Ni/Ti multilayer catalyst for growing CNTs. They mentioned that modifying the structure into a double catalytic layer structure and adding Al as a barrier layer helps to improve the uniformity of the surface metal nanoparticle catalyst distribution, eventually leading to uniformly distributed vertically aligned CNTs synthesized at low temperatures. Based on the previous work discussed, in this work, we use a double catalytic layer with an additional Al layer to demonstrate the potential to grow higher quality CNTs at low temperatures. Similarly, in this work, we will demonstrate that the use of Co metal for the double catalytic layer can result in a lower I_D/I_G ratio for the growth of CNTs at low temperatures. Later in our study, we also investigated the electrical resistance and thermal conductivity of the grown CNTs. Modifying the structure into a double catalytic layer structure and adding Al as a barrier layer helped to improve the uniformity of the surface metal nanoparticle catalyst distribution, eventually leading to uniformly distributed vertically aligned CNTs synthesized at low temperatures.

2. Materials and Methods

p-type Si (100) wafers with a substrate area of 2 cm × 2cm were used (JunSun, Taipei, Taiwan). To ensure the cleanliness of the samples, the surface was cleaned in an ultrasonic cleaner with acetone, isopropanol, and DI water. Next, we put the silicon substrate on a heater for 10 min to ensure that no excess water was on the surface. Metal films consisting of 100 nm Ti, 2 nm Co, 10 nm Al, and 2 nm Co layers were sputtered onto the silicon substrate using direct current (DC) sputtering and used as the single catalytic layer and double catalytic layer structure. Subsequently, we placed the sputter-coated samples into a TCVD furnace (JunSun, Taipei, Taiwan) for CNT growth. In the heating stage, using 500/30 standard cubic centimeters per minute (sccm) of Ar/H_2, the samples were heated up to 350~400 °C. Upon reaching the growth temperature, we replaced the Ar/H_2 with C_2H_2 at 180 sccm for 30 min for all the fabricated samples. The grown CNT samples were characterized using a JSM-6390 scanning electron microscope (SEM, Contrel Technology Co., Ltd., Taipei, Taiwan), a Hitachi H-7100 transmission electron microscope (TEM, Materials Analysis Technology Inc., HsinChu, Taiwan), a Keithley 2400 I–V measurement system (Agilent Technologies, NYSE:A, HsinChu, Taiwan), and Raman spectrometer (Materials Analysis Technology Inc., New Taipei city, Taiwan) with a 532 nm Ar^+ laser.

3. Results and Discussion

3.1. Structural Analysis and Surface Quality Performance

As shown in Figure 1a, the use of a double catalytic layer has the advantage of increasing the concentration of surface catalytic particles and has the potential to facilitate the growth of CNTs at low temperatures. CNT growth was carried out on a p-Si substrate coated with Ti (100 nm), Co (2 nm), Al (10 nm), and Co (2 nm) (as shown in Figure 1b), and other single catalytic layer samples were prepared with the same catalyst thickness and used as a comparison. Initially, we compared CNTs grown using Ni and Co as catalytic layer materials and found that CNTs grown using Co as the catalytic layer had a higher tendency for growth.

Therefore, we compared single catalytic layers and double catalytic layers using Co as the substrate and found that at a low temperature of 400 °C, CNTs grown using a double catalytic layer structure on a Co substrate had a height of 1.97 µm. Compared with the height of CNTs grown using a single catalytic layer, the height of CNTs grown using a double catalytic layer on a Co substrate increased by approximately 7.9-fold (Figure 2a). The addition of an Al barrier layer to create a Co-Al layer was found to be effective in reducing the diffusion of Co and minimizing interactions, leading to a notable increase in the height of CNTs. Besides, adding another layer of Co effectively increases the concentration of Co particles, resulting in the growth of well-aligned and denser nanotubes. Therefore, we conclude that a double catalytic layer has the characteristics of optimizing the growth height of CNTs grown using Co as the catalytic layer material. In Figure 2b, electron microscopy images (90° tilted) of CNTs grown on the substrate at a temperature of 400 °C for Co/Al/Co/Ti multilayers are shown. It can be seen from the SEM images that the arrangement is neat and dense. The inset TEM image of CNTs grown at 400 °C indicates that the CNTs appear to be hollow. For our sample, the average diameter was found to be around 13 nm.

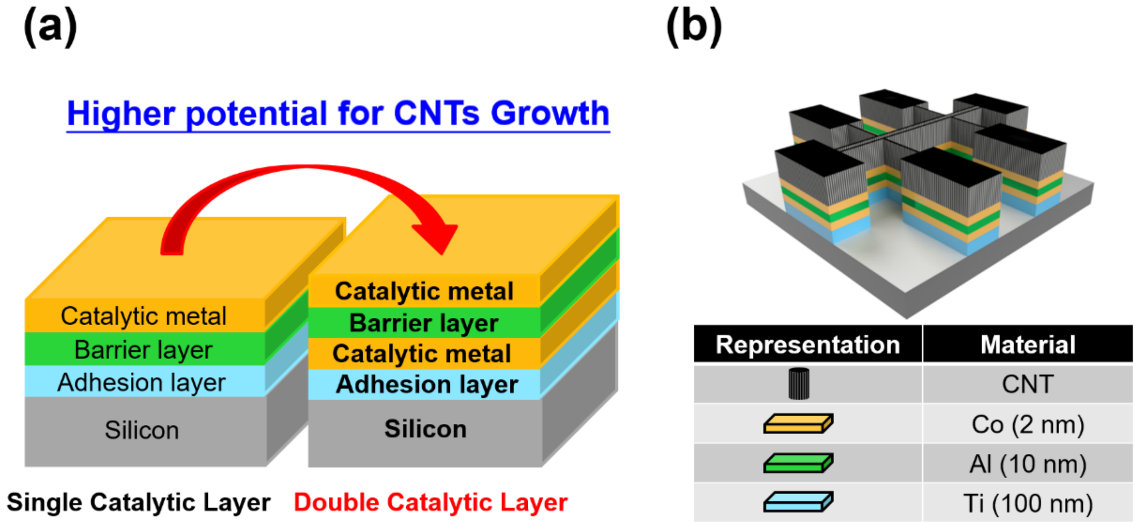

Figure 1. (**a**) The modification of the carbon nanotube growth structure to a double catalytic layer, which has higher potential for low temperature growth of CNTs. (**b**) Schematics of vertical CNTs grown on a Si substrate with a catalytic metal under-layer.

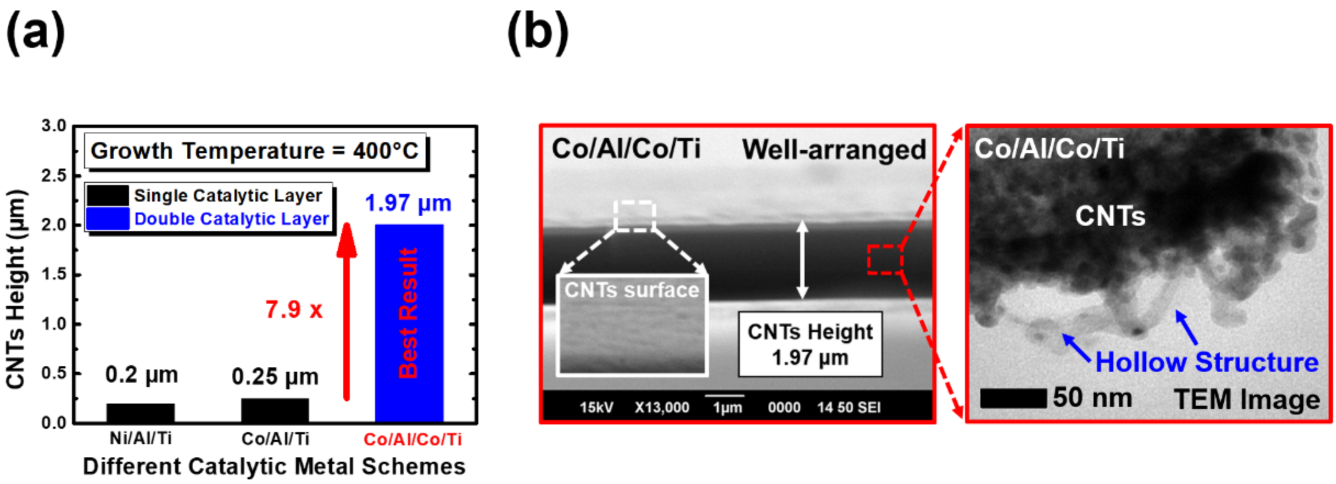

Figure 2. (**a**) Comparison of the heights of CNTs grown on single catalytic layer and double catalytic layer. (**b**) Transmission electron microscopy and electron microscopy images of the CNT grown at 400 °C. The images show the CNT has good density and material quality.

Next, we focus on the quality of the CNTs grown by using double catalytic layers, as shown in Figure 3. We compared the Raman spectra to assess the quality and the I_D/I_G ratio of the CNTs grown using different catalytic layers at 400 °C. The results show that the double catalytic layer has a lower I_D/I_G ratio compared to the single catalytic layer, indicating higher CNT quality [13]. The I_D/I_G ratio of 0.92 for the double catalytic layer represents a higher surface growth quality compared to the I_D/I_G ratio of 1.05 for the single catalytic layer.

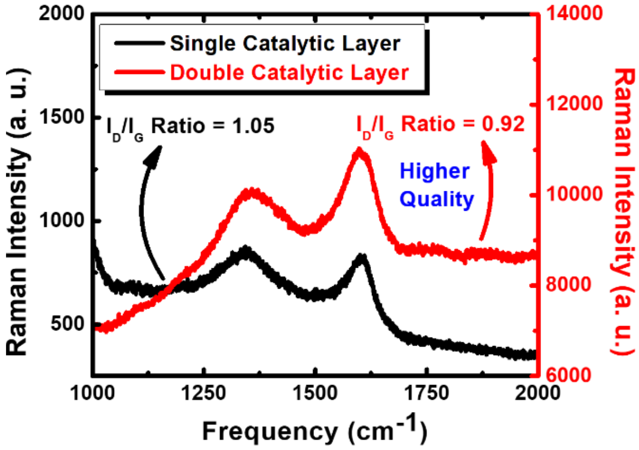

Figure 3. I_D/I_G ratio data from the Raman spectroscopy of the CNTs grown at 400 °C. The results demonstrate that the double catalytic layer exhibits a superior surface quality.

Figure 4a compares the I_D/I_G ratio of the CNTs grown using a Co/Al/Co/Ti double catalytic layer at 400 °C and 350 °C using Raman spectroscopy. The I_D/I_G ratio was found to be 0.92 at 400 °C and 0.98 at 350 °C, indicating a higher CNT quality at 400 °C. In Figure 4b, the I_D/I_G ratio is compared to other works using Co as the metal catalyst material [9,11,14,15]. The results show that the I_D/I_G ratio is lowest at 350 °C and relatively low at 400 °C, indicating that the low-temperature growth of nanotubes is feasible and has reached a certain level in this work.

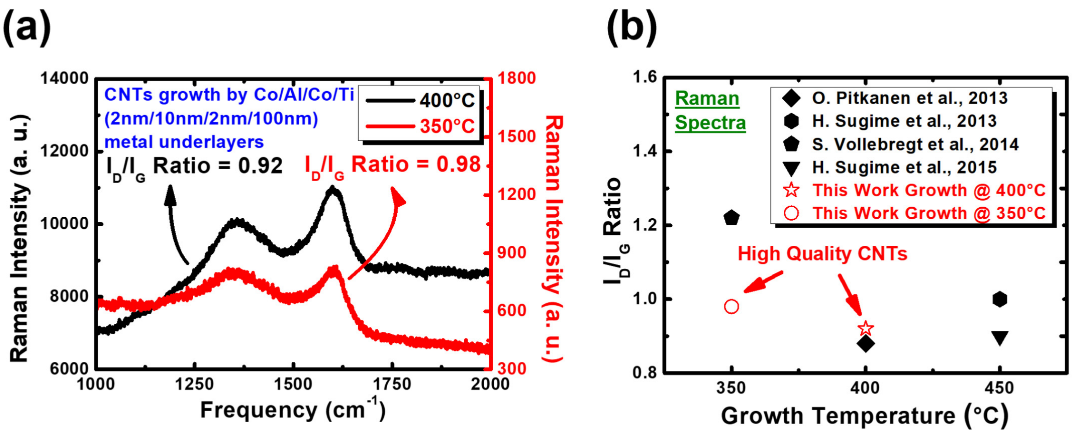

Figure 4. (**a**) The quality of CNTs grown on a Co/Al/Co/Ti structure, as evaluated by Raman spectroscopy at growth temperatures of 400 °C and 350 °C. (**b**) Comparison of the I_D/I_G ratio obtained from Raman spectroscopy with values reported in the literature. A lower I_D/I_G ratio indicates the good quality of the CNTs [9,11,14,15].

Based on the combined results of the Raman spectroscopy analysis and TEM images, it can be concluded that the growth of CNTs exhibits a certain level of high quality. This is indicated by the proximity of the D peak and G peak values in the Raman spectra. Furthermore, the I_D/I_G ratio confirms that the CNTs are multi-walled in structure. Based on their characteristics, the CNTs can be classified as mixed type, incorporating both metallic and semiconductor properties.

3.2. Electrical and Thermal Performance of CNTs

Figure 5a shows the I–V characteristic measurements of the electrical resistance (R) of CNTs grown using a Co-based catalytic layer and compares them with those reported in the literature [9,11,15,16]. The lowest R among the CNTs grown in this study was observed at 400 °C, as demonstrated by the graph, with the minimum value representing an impressively low R of 128 Ω. In contrast, the R at 350 °C is 22.15 kΩ, indirectly indicating that the grown CNTs exhibit an excellent electrical performance. The experimental results suggest that the use of a Co-based catalytic layer can effectively enhance the electrical properties of CNTs. To investigate the heat dissipation performance of CNTs, we conducted measurements using the commonly used 3-omega method [17]. In Figure 5b, the measured k values were found to be 11.7 (W/mK) and 29.8 (W/mK) at 400 °C and 350 °C, respectively. Compared with the k value reported by H. Sugime et al. [11], the observed k values in our study reveal considerable advantages, signifying a superior heat dissipation performance.

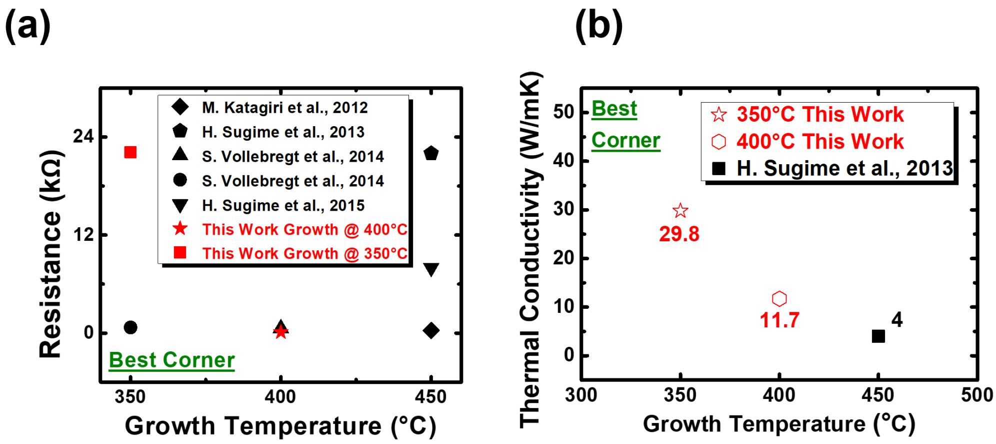

Figure 5. (**a**) Comparison of the resistance values obtained in this study with those reported in the literature [9,11,15,16]. (**b**) Thermal conductivity (k) value comparison of CNTs grown at low temperature in this work with the one reported in the literature [15].

Integrating all the comparative numerical values and highlighted results, the following Table 1 presents the summarized results.

Table 1. Comparison of Low-Temperature Growth of Carbon Nanotubes with a Co Catalyst.

Reference	Growth Temperature (°C)	I_D/I_G Ratio	Resistance (kΩ)	Thermal Conductivity (W/mK)
[9]	350/400	1.22/-	0.691/0.583	-
[11]	450	0.9	8	4
[14]	400	0.88	-	-
[15]	450	1	22	-
[16]	450	-	0.323	-
This work, growth @ 400 °C	400	0.92	0.128	11.7
This work, growth @ 350 °C	350	0.98	22.15	29.8

4. Conclusions

In summary, this work demonstrates the growth of high-quality CNTs at a low temperature of 350 °C using a double catalytic layer. The use of Co-based metal catalysts is shown to be beneficial for CNT growth, and the adoption of a double catalytic layer results in higher-quality CNTs at low temperatures. Compared to our previous work [5], the CNTs grown in this work are higher (CNT height = 1.97 µm), making them more versatile for applications in various fields. Additionally, a Raman spectra analysis confirmed their high-quality performance index (I_D/I_G ratio = 0.92 at 400 °C and I_D/I_G ratio = 0.98 at 350 °C). I–V characteristic measurements indicated the excellent electrical performance of the grown CNTs (the lowest R obtained was 128 Ω at 400 °C). Finally, the k values measured using the 3-omega method indicate a superior heat dissipation performance compared to other studies in the literature (11.7 W/mK for CNTs grown at 400 °C and 29.8 W/mK for CNTs grown at 350 °C), indicating their potential for advanced packaging and power applications in the future. The low-temperature grown CNTs in this study exhibit significant advantages compared to those in the international literature. The lower I_D/I_G ratio indicates a lower defect density in the CNTs, while the lower electrical resistivity and higher thermal conductivity indicate their enhanced transmission rate and heat dissipation performance, making them more effective for future packaging applications.

Author Contributions: Conceptualization, M.-H.L. (Min-Hung Lee), M.-H.L. (Ming-Han Liao) and H.-Y.L.; methodology, H.-Y.L.; formal analysis, H.-Y.L.; investigation, H.-Y.L.; resources, M.-H.L. (Min-Hung Lee), S.-C.C. and M.-H.L. (Ming-Han Liao); writing—original draft preparation, H.-Y.L.; writing—review and editing, H.-Y.L. and N.B.; supervision, M.-H.L. (Ming-Han Liao). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Technology (MOST), Taiwan, under grants 109-2628-E-002-003-MY3 and 111-2218-E-002-040-MBK. This work was also supported by the Ministry of Education, Taiwan, under grants 110L892605, 110L7728, and 110HT512004.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Experimental data can be available by contacting the author.

Acknowledgments: The authors thank S.-C.C. from Ming Chi University of Technology for their technical support with the Raman spectroscopy analysis. The discussions and project funding support from industry (Intel and PSMC) are also highly appreciated.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kim, P.; Shi, L.; Majumdar, A.; McEuen, P.L. Thermal transport measurements of individual multiwalled nanotubes. *Phys. Rev. Lett.* **2001**, *87*, 215502. [CrossRef] [PubMed]
2. Wei, B.; Vajtai, R.; Ajayan, P. Reliability and current carrying capacity of carbon nanotubes. *Appl. Phys. Lett.* **2001**, *79*, 1172–1174. [CrossRef]
3. Ahmad, M.; Silva, S.R.P. Low temperature growth of carbon nanotubes—A review. *Carbon* **2020**, *158*, 24–44. [CrossRef]
4. Lu, P.-Y.; Yen, C.-M.; Chang, S.-Y.; Feng, Y.-J.; Lien, C.; Hu, C.-W.; Yao, C.-W.; Lee, M.-H.; Liao, M.-H. The demonstration of Carbon Nano-Tubes (CNTs) as a promising high Aspect Ratio (>25) through silicon vias (TSVs) material for the vertical connection in the high dense 3DICs. *IEEE IEDM* **2020**, *121*, 232101.
5. Lin, H.-Y.; Basu, N.; Chen, S.-C.; Lee, M.-H.; Liao, M.-H. The demonstration of low-temperature (350 °C) grown Carbon Nano-Tubes for the applications of through silicon via in 3D stacking and Power-Via. *Appl. Phys. Lett.* **2022**, *121*, 232101. [CrossRef]
6. Fouquet, M.; Bayer, B.C.; Esconjauregui, S.; Blume, R.; Warner, S.; Hofmann, R.; Schlögl, C.; Thomsen, J. Highly chiral-selective growth of single-walled carbon nanotubes with a simple monometallic Co catalyst. *Phys. Rev. B* **2012**, *85*, 235411. [CrossRef]
7. Jourdain, V.; Bichara, C. Current understanding of the growth of carbon nanotubes in catalytic chemical vapor deposition. *Carbon* **2013**, *58*, 2–39. [CrossRef]
8. Ding, F.; Larsson, P.; Larsson, J.A.; Ahuja, R.; Duan, H.; Rosén, A.; Bolton, K. The importance of strong carbon− metal adhesion for catalytic nucleation of single-walled carbon nanotubes. *Nano Lett.* **2008**, *8*, 463–468. [CrossRef]
9. Vollebregt, S.; Tichelaar, F.; Schellevis, H.; Beenakker, C.; Ishihara, R. Carbon nanotube vertical interconnects fabricated at temperatures as low as 350 °C. *Carbon* **2014**, *71*, 249–256. [CrossRef]
10. Xiao, Y.; Ahmed, Z.; Ma, Z.; Zhou, C.; Zhang, L.; Chan, M. Low temperature synthesis of high-density carbon nanotubes on insulating substrate. *Nanomaterials* **2019**, *9*, 473. [CrossRef]
11. Sugime, H.; Esconjauregui, S.; D'Arsié, L.; Yang, J.; Robertson, A.W.; Oliver, R.A.; Bhardwaj, S.; Cepek, C.; Robertson, J. Low-temperature growth of carbon nanotube forests consisting of tubes with narrow inner spacing using Co/Al/Mo catalyst on conductive supports. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16819–16827. [CrossRef] [PubMed]
12. Li, S.; Raju, S.; Zhou, C.; Chan, M. Carbon nanotube contact plug on silicide for CMOS compatible interconnect. *IEEE Electron Device Lett.* **2016**, *37*, 793–796. [CrossRef]
13. Chhowalla, M.; Teo, K.; Ducati, C.; Rupesinghe, N.; Amaratunga, G.; Ferrari, A.; Roy, D.; Robertson, J.; Milne, W. Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition. *J. Appl. Phys.* **2001**, *90*, 5308–5317. [CrossRef]
14. Pitkänen, O.; Halonen, N.; Leino, A.-R.; Mäklin, J.; Dombovari, A.; Lin, J.; Toth, G.; Kordás, K. Low-temperature growth of carbon nanotubes on bi-and tri-metallic catalyst templates. *Top. Catal.* **2013**, *56*, 522–526. [CrossRef]

15. Sugime, H.; Esconjauregui, S.; Yang, J.; D'Arsié, L.; Oliver, R.A.; Bhardwaj, S.; Cepek, C.; Robertson, J. Low temperature growth of ultra-high mass density carbon nanotube forests on conductive supports. *Appl. Phys. Lett.* **2013**, *103*, 073116. [CrossRef]
16. Katagiri, M.; Wada, M.; Ito, B.; Yamazaki, Y.; Suzuki, M.; Kitamura, M.; Saito, T.; Isobayashi, A.; Sakata, A.; Sakuma, N. Fabrication and characterization of planarized carbon nanotube via interconnects. *J. Appl. Phys.* **2012**, *51*, 05ED02. [CrossRef]
17. Kumanek, B.; Janas, D. Thermal conductivity of carbon nanotube networks: A review. *J. Mater. Sci.* **2019**, *54*, 7397–7427. [CrossRef]