Contact Behavior among Vertically Aligned Carbon Nanotube Bumps under Compression for Flexible Multilayer Substrates

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Vertically aligned carbon nanotubes (VACNTs) are promising candidates as vertical interconnects in multilayer substrates. Therefore, VACNTs were applied to the via structure in a multilayer flexible substrate as flexible bumps by surface activated bonding indeed. During the manufacturing process, VACNT bumps were compressed and deformed by the bonding pressure. In this research, VACNT deformation and structural mechanics were evaluated and analyzed under compression by an indenter. VACNT bumps were compressed to about 20% of their original height as multiple VACNT bundles folded under pressure more than 0.40 MPa. The VACNT compression height depended on the bonding pressure, which was within the range 0.04 to 0.20 MPa. Moreover, it was concluded that friction force between neighboring VACNTs caused plastic deformation of the VACNT bundles.

Flexible assembly technology is one of the key factors for the development of modern electronics devices. This technology incorporates weight reduction, roll-to-roll technology for decreased production cost, reduction of mechanical stress caused by plastic deformation for die attachment or flip chip interconnects, and the application for wearable devices. High-density multilayer integration for flexible substrates provides miniaturization, high performance, and multi-functionalization of devices. To achieve multilayer assembly of flexible substrates, interlayer connections are required for electrical contact between each layer and mechanical robustness. Metal nanoporous structures like adhesive silver paste1 or structures produced by de-alloying and extracting one component from an alloy2–7 possess the properties of electrical contact and robustness against mechanical deformation.

On the other hand, carbon nanotubes (CNTs) are a popular solution for flexible interconnects. CNTs are expected to be a substitutional wiring material for copper because of their high maximum allowable current density of 10,000 A/cm² estimated from ion beam irradiation.8 CNTs can be constructed in vertically aligned structures by controlling the catalyst density and synthesis condition.9 Vertically aligned carbon nanotubes (VACNTs) can serve as via structures by metal deposition on top of the VACNTs.10 VACNT bundles consist of entwined and nominally vertical carbon nanotubes which have the attractive material properties of compressibility and flexibility.11,12 Horizontal CNT wirings can also be obtained through use of horizontally grown CNTs13 that are subsequently connected with metal electrodes.14

CNTs are typically synthesized by the thermal chemical vapor deposition (CVD) method at temperatures exceeding 500°C. In order to avoid this high temperature process, VACNTs are transferred after synthesis to other substrates by using thermocompression,15 an adhesive conducting polymer,16 a solder alloy,17 or an adhesive conducting metal.18 For the thermocompression bonding method, the top surface of the VACNTs is coated by a metal and bonded to a metallic substrate at 150°C for 2 h.11

Separately, the surface activated bonding (SAB) method uses Ar-fast atom bombardment (Ar-FAB) as a dry process with complete and immediate bonding and the added advantage of alignment. Moreover, the contact resistance between VACNTs and metals can be reduced by irradiation damage from Ar-FAB.20

Applying these techniques, we fabricated flexible multilayers using VACNT bumps to yield flexible device characteristics.21 However, fabrication requires transfer of VACNT bumps with appropriate axial force.21 As a result, the compression deforms and buckles VACNT bundles which leads to unique properties that depend on the interactions between individual VACNTs.22,23 An understanding of the compression behavior of VACNTs is required for fabrication of VACNTs as vertical interconnects. We report the fabrication of flexible multilayer substrates with VACNT bumps and evaluate their behavior by considering the friction among CNTs during compression.

Fabrication Process of Flexible Multilayer Substrates with VACNT Bumps

The fabrication process of VACNT bump vias in flexible multilayer substrates is shown in Fig. 1.21 At first, 100 μm tall VACNT bundles were synthesized at 600–800°C from a pre-deposited catalyst layer patterned on a Si substrate (Fig. 1(b)). A polypime substrate with a 20 μm deep via hole structure was patterned with photolithography and etching (Fig. 1(a)). The VACNT substrate was prepared with a size of 6 × 6 mm² and individual VACNT bump patterns were 200 μm in diameter. Then, Au was sputtered on the surfaces of both the etched polypime substrate and the synthesized VACNT substrate (Figs. 1(2a) and (2b)). Au-sputtered substrates were bonded after a 30 s Ar plasma activation under a load of 0.36 MPa at 150°C (Fig. 1(c)). The bonding process was performed with an Ar plasma activated bonding apparatus with a two-sight camera unit, bonding head, and a heated stage for precise alignment and bonding.25 After the first bonding process, the Si growth substrate was lifted-off with tweezers from the polypime substrate while transferring VACNT bundles into via hole structures on the polypime substrate (Fig. 1(d)). Then, Au was sputtered on the side lifted off the polypime substrate with VACNT bumps (Fig. 1(5)). The substrate with VACNTs was bonded to the second polypime substrate with a Au layer by plasma activated bonding with a load of 1.2 MPa at 150°C (Fig. 1(6)). After the second bonding, the first polypime substrate was etched away and the etched polypime substrate with circuit patterns was sputtered with Au again. These substrates were then bonded to finish the fabrication process flow. The precise fabrication process was described in our previous work.21 Fabrication of these two-layer substrates demonstrates the concept for flexible multilayer substrates with VACNT bumps. As such, these etching, sputtering, and bonding processes can be repeated several times for multilayer devices.

Compression Evaluation of VACNT Bumps

We succeeded in fabricating flexible multilayer substrates with VACNT bump vias. In our previous work,21 the resistance of VACNT bumps was found to be related to the compression load during the bonding process. Therefore, the structural deformation of VACNT bumps was analyzed. When a substrate with VACNT bumps was compressed, the VACNT compression height depended on the bonding pressure, which was within the range 0.04 to 0.20 MPa. Moreover, it was concluded that friction force between neighboring VACNTs caused plastic deformation of the VACNT bundles.

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was bonded with another substrate using the SAB method, a steep decrease in the height of the VACNT bumps was observed.\textsuperscript{20}

In this section, the deformation of the VACNT bumps under compression was investigated. A uniaxial compression test was performed with a micro-strain tester (Shimadzu MST-I). A substrate with VACNT bumps was set on a Si substrate with VACNT grown tip down and the indenter compressed the VANCNT bump perpendicular behind the growth substrate (Fig. 2a).

Uniform perpendicular compression was applied over the VACNT bumps with pressures from 0.2 to 1.0 MPa. Detailed views of the VACNT bumps before and after compression are shown in the scanning electron microscope (SEM) images in Figs. 3a–3c. The VACNT bumps have such high compressibility that their height decreased from 100 to 18–68 \( \mu \text{m} \) under applied pressures of 0.2 to 1.0 MPa. The VACNT bumps retained their cylindrical shape without lateral swelling, which highlights the utility of CNTs as a material for bumps or vias in circuits. However, a large lateral distortion was observed in VACNT bumps with excessive pressures of 1.0 MPa (Fig. 3c). The height of the VACNT bump after each compression was measured with confocal microscopy as shown in Fig. 3d. The measurement showed an abrupt decrease in the height of VACNT bumps with an increasing applied pressure around 0.3 MPa. The height of VACNT bumps was reduced to 25 \( \mu \text{m} \) until the applied pressure reached 0.6 MPa. Further increasing the applied pressure caused the VACNT bumps to remain at an almost constant height of 20 \( \mu \text{m} \). However, the VACNT bump compressed at 0.6 MPa appeared folded at a height of 20 \( \mu \text{m} \). Further, the VACNT bump compressed at 1.0 MPa was distorted.
from the folded morphology at the same height due to excessive pressure.

Fig. 4 shows the compressed VACNT bundles at pressures up to 0.2 MPa. For observing these compressed VACNT bundles, VACNTs grown over a larger area (ca. 200 mm²) were used for controlling the compression load. In Fig. 4a, whole VACNT bundles were standing almost vertically against substrate without compression load. VACNT bundles near the growth substrate were bent slightly after 0.04 MPa compression (Fig. 4b), and were folded as “S” shape after 0.12 MPa (Fig. 4c). The number of VCNT folds increased with increasing compression load reaching four folds after a compression of 0.2 MPa (Fig. 4d). VACNT bumps did not recover their original morphology six months after the compression.

Nano-indentation measurements were performed with a Shimadzu DUH-W201S to obtain stress-strain curves of VACNT bundles (Fig. 2b). A frustoconical indenter equipped with a 500 µm flat tip was applied for the measurement. In Fig. 5a, each stress-strain curve corresponds to each compression load. These load curves consist of the first sharp inclination at 0–1 mN, the first gentle inclination at 1–7 mN, the second sharp inclination at 7–9 mN, and the second gentle inclination at pressures exceeding 9 mN. The unload curves show plastic deformation with a large load compression of more than 2 mN. Fig. 5b shows the schematic folding model of compressed VACNT bundles, which is estimated from both the cross-sectional images in Fig. 4 and the stress-strain curves in Fig. 5a. The stress-strain curves indicate the axial compression sequence of the VACNT bundles. Under forces below 1 mN, VACNT bundles are compressed with elastic strain (Figs. 5b[A] and 5b[B]) with slight plastic deformation (Fig. 5b[C]). VACNT bundles on the substrate side are bent and folded under a 1–7 mN compression load (Fig. 5b[D]). Once folded, the VACNT bundles are unloaded, their folded area is irreversibly compressed, and the unfolded area is elastically uncompressed (Figs. 5b[D] and 5b[E]). Consequently, the folding of the VACNT bundles developed continuously into multiple foldings while the unfolded area remained elastic (Figs. 5b[F] and 5b[G]).

**Folding of VACNT Bundles under Compression**

The folded area of the VACNT bundles shows irreversible deformation under high compression. In this section, we discuss the friction force among CNTs as the cause of this irreversible deformation.

The contacts between neighboring CNTs generate van der Waals forces, which can be considered friction in classical mechanics. Calculating friction forces would be difficult due to randomly oriented VACNTs before plastic deformation occurs (Fig. 6a). Since CNTs fold in one lateral direction after buckling initiation, it is simpler to calculate friction forces between neighboring CNTs due to van der Waals forces. Therefore, the model for calculating friction forces in VACNTs is given in Fig. 6c. The model relies on the SEM image of VACNT bumps after compression (Fig. 6b) in which the diameter and pitch of CNTs is 30 and 100 nm, respectively. In addition, there are 10 sine waves with a length of 10 µm in one CNT and its amplitude is set equal to 40 nm in the initial state from Fig. 6a. Alignment, density, and radius will all affect the mechanical behavior of VACNT bumps. As such, the individual values obtained from this model will be less useful but we expect to elucidate the effect of friction forces between neighboring CNTs on the behavior of VACNTs.

First, individual CNTs are elastic with their ends loosely pinned by van der Walls forces. Based on this model, we consider the elastic buckling of a column as the behavior of an individual CNT with an initial displacement, \(v_0\), which is given as

\[
E I \frac{d^2v}{dx^2} + P(v + v_0) = 0
\]

**Figure 4.** Cross-sectional SEM images of compressed VACNT bundles (a) without load, (b) after 0.04 MPa compression load, (c) after 0.12 MPa compression load, and (d) 0.2 MPa compression load.

**Figure 5.** (a) Stress-strain curves of VACNT bundles with 1 to 10 mN load. (b) Folding model of compressed VACNT bundles. Indexes [A]–[G] correspond to each stress-strain phase.

**Figure 6.** SEM images of (a) as grown VACNT bundles and (b) VACNT bundles after 0.4 MPa compression. (c) A model of a VACNT with sine curve shape estimated from compressed VACNT bundles.
where $E$ is the Youngs modulus, $I$ is the second moment of area, $P$ is the applied force, and $\nu$ is the lateral displacement. Assuming the initial displacement is a sine wave with an amplitude of $a$:

$$v_0 = a \sin \frac{\pi x}{L} \quad [2]$$

This gives a general solution:

$$v = A \sin kx + B \cos kx + \frac{P}{(\pi/L)EI} - P \cdot a \sin \frac{\pi x}{L} \quad [3]$$

The boundary conditions are as follows: $v = 0$ for $x = 0, L$, then $A = B = 0$ and the equation reduces to

$$v = \frac{P}{P_{cr}} - P \cdot a \sin \frac{\pi x}{L} \quad [4]$$

where $P_{cr} = \pi^2 EI/L^2$, which is called Euler’s buckling load formula. The maximum displacement $v_{max}$ for $x = L/2$ is written as

$$v_{max} = a \cdot \frac{P}{P_{cr} - \frac{P}{a}} \quad [5]$$

Accordingly the maximum load as a function of $v_{max}$ is given by

$$P = P_{cr} \cdot \frac{v_{max}/a}{1 + v_{max}/a} \quad [6]$$

Moreover, the load distribution is derived from the maximum load multiplied by $\sin \theta$:

$$P = P_{cr} \cdot \frac{v_{max}/a}{1 + v_{max}/a} \cdot \sin \theta \quad [7]$$

As shown in Figs. 3 and 4, the deformation of VACNT bundles continued after removing axial pressure, and recovery did not occur even after several weeks. By applying this model to neighboring CNTs in the same plane, friction forces among the neighboring CNTs were calculated. CNTs are compressed vertically and expand laterally with the applied load. As a result, contacts between neighboring CNTs cause the load to be distributed at each location in accordance with the displacement. The difference between the two loadings on each CNT produces the friction force. This force may be responsible for permanent fixation of VACNT bumps following compression.

According to previous studies, we assumed that the longitudinal stiffness of identical CNTs was 1.06 TPa and the static friction coefficient was 0.9. The longitudinal stiffness should be theoretically close to the graphene in-plane modulus. Many experiments were performed to yield a value approximately equal to the theoretical data. The friction force distributed over contact points among neighboring folded VACNTs was calculated. The contact area among CNTs during compression was geometrized from Fig. 3c, and the friction force at each point of one folded and sine-curved VACNT was calculated by applying Equation 7. The results of which are shown in Fig. 7. When CNTs were compressed from 10 to 4 µm, the friction force at each contact point among neighboring folded VACNTs reached about 1.7 nN along each individual wavelength. Furthermore, the friction force among neighboring VACNTs of each compression ratio was calculated from the integration of the friction force at each contact point shown in Fig. 7, and the result shows in Fig. 8. Fig. 8 shows the relation between compression ratio of VACNTs and friction forces among neighboring VACNTs. The friction force was generated at 55% of compression ratio, and increased with increasing compression ratio of VACNTs.

These calculations of compression depth correspond well with the results of the nano-indentation measurements. From Fig. 5, the compression depth for each fold was 6 to 8 µm, which corresponds to a compression ratio of 60 to 80% for each wavelength of a VACNT.

The folding or buckling of VACNTs was also observed and analyzed previously. The structure and morphology of individual VACNTs and the geometry of grown VACNTs comprise the contributing factors in the strain-stress properties of a CNT array.

In this research, the geometric parameter of VACNTs was extracted from the cross-sectional SEM images of VACNT bundles. Therefore, the compression ratio in folded VACNT bumps should vary depending on the growth condition. The model of the friction force among VACNTs was developed in compliance with the compression behavior of the VACNT array.

**Conclusions**

In this research, flexible VACNT bumps are used as vertical interlayer interconnects in multilayer flexible substrates. The polymer flexible multilayer substrates are fabricated by the SAB method. Plastic deformation of the VACNT bumps occurred through axial compression during bonding process. Therefore, we evaluated and analyzed the mechanical structure and properties of the VACNT bumps under compression. The compression of VACNT bumps was derived from the multiple folding of VACNT bundles. The bump was compressed to about 20% of the original height with axial pressures larger than 0.40 MPa. Under 0.20 MPa, the compressed height corresponded to the folding of the VACNT bundles which depended on the axial pressure. The compression deformation remained after removing the pressure. This observation was rationalized by considering the friction force among neighboring VACNTs in contact with each other.
during compression. As such, the compression pressure controlled the deformation of the VACNT bumps. We hypothesize that the density and initial structure of the VACNTs are also key factors for the deformation of VACNT bumps.

References

1. Y. Li, K. Moon, and C. P. Wong, Nano-Bio-Electronic, Photonic and MEMS Packaging, p. 19, Springer, New York (2010).
2. L. Liu, E. Pippel, R. Scholz, and U. Gsele, Nano Lett., 9, 4352 (2009).
3. C. Zhao, Z. Qi, X. Wang, and Z. Zhang, Corrosion Science, 51, 2120 (2009).
4. X. Wang, W. Wang, Z. Qi, C. Zhao, H. Ji, and Z. Zhang, J. Alloy. Compounds, 508, 463 (2010).
5. H. Oppermann and L. Dietrich, Microelectron. Reliab., 52, 356 (2012).
6. H. Mimatsu, T. Kasahara, M. Saito, H. Nishikawa, and S. Shoji, Jpn. J. Appl. Phys., 52, 030204 (2013).
7. W. S. Wang, Y. C. Lin, T. Gessner, and M. Esashi, Jpn. J. Appl. Phys., 54, 030215 (2015).
8. B. Q. Wei, J. D’Arcy-Gall, P. M. Ajayan, and G. Ramanath, Appl. Phys. Lett., 83, 3581 (2003).
9. D. Kondo, S. Sato, A. Kawabata, and Y. Awano, Nanotechnology, 19, 435601 (2008).
10. Y. Awano, S. Sato, D. Kondo, M. Ohfuti, A. Kawabata, M. Nihei, and N. Yokoyama, physica status solidi A., 203, 3611 (2006).
11. R. D. Johnson, D. F. Bahr, C. D. Richards, R. F. Richards, D. McClain, J. Green, and J. Jiao, Nanotechnology, 20, 065703 (2009).
12. K. P. Young, J. Wei, and B. K. Toy, Diamond Rel. Mater., 18, 1109 (2009).
13. Y. Chai, Z. Xiao, and P. C. H. Chan, Nanotechnology, 21, 235705 (2010).
14. N. Chiadarelli, A. Fournier, H. Okuno, and J. Dijon, Carbon, 60, 139 (2013).
15. X. Song, Z. Gan, S. Liu, H. Yan, and Q. Lv, J. Appl. Phys., 106, 104308 (2009).
16. H. Jiang, L. Zhu, K. Moon, and C. P. Wong, Nanotechnology, 18, 125203 (2007).
17. A. Kumar, V. L. Pushparaj, S. Kar, O. Nalamasu, P. M. Ajayan, and R. Baskaran, Appl. Phys. Lett., 89, 163120 (2006).
18. I. Soga, D. Kondo, Y. Yamauchi, T. Iwai, M. Mizukoshi, Y. Awano, K. Yube, and T. Fujii, in Proc. 58th ECTC, Florida, USA, pp. 1390 (2008).
19. C. Lan, P. Srisungsitthiunt, P. B. Amama, T. S. Fisher, X. Xu, and R. G. Reifenberger, Nanotechnology, 19, 125703 (2008).
20. M. Fujino, I. Soga, D. Kondo, Y. Ishizuki, T. Iwai, and T. Suga, Microelectron. Reliab., 55, 2560 (2015).
21. M. Fujino, H. Terasaka, and T. Suga, Jpn. J. Appl. Phys., 54, 030205 (2015).
22. A. Hamdan, J. Cho, R. Johnson, J. Jiao, D. Bahr, R. Richards, and C. Richards, Nanotechnology, 24, 015702 (2013).
23. A. Cao, P. L. Dickrell, W. G. Sawyer, M. N. Ghasemi-Nejad, and P. M. Ajayan, Science, 310, 1307 (2005).
24. A. A. Zhlob, S. D. Mesarovic, E. T. Lilleodden, D. McClain, J. Jiao, and D. F. Bahr, Nanotechnology, 19, 175704 (2008).
25. T. Suga, T. Itoh, Z. Xu, M. Tomita, and A. Yamauchi, Proc. 52nd Electronic Components and Technology Conference, pp. 105 (2002).
26. R. S. Ruoff, J. Tersoff, D. C. Lorentz, S. Subramoney, and B. Chan, Lett. Nature, 364, 514 (1993).
27. S. D. Mesarovic, C. M. McCarter, D. F. Bahr, H. Radhakrishnan, R. F. Richards, C. D. Richards, D. McClain, and J. Jiao, Scripta Materialia, 56, 157 (2007).
28. A. E. H. Love, A Treatise on the Mathematical Theory of Elasticity, 4th ed., p. 399, Dover Publications, New York (1944).
29. J. Zhao and J. Zhu, Micron, 42, 663 (2011).
30. P. L. Dickrell, S. K. Pal, G. R. Bourne, C. Muratore, A. A. Voevodin, P. M. Ajayan, L. S. Schadler, and W. G. Sawyer, Tribology Lett., 24, 85 (2006).
31. W. Ding, L. Calabri, K. M. Kohlhaas, X. Chen, D. A. Dikin, and R. S. Ruoff, Exp. Mech., 47, 25 (2007).
32. Y. Li, J. Kang, J.-B. Choi, J.-D. Nam, and J. Suhr, Nanotechnology, 26, 245701 (2015).
33. P. Fraternali, J. R. Raney, and C. Daraio, Composite Structures, 96, 745 (2013).
34. J. Zhao, M.-R. He, S. Dai, J.-Q. Huang, F. Wei, and J. Zhu, Carbon, 49, 206 (2011).
35. F. Fraternali, A. A. Zbib, S. D. Mesarovic, E. T. Lilleodden, D. McClain, J. Jiao, and D. F. Bahr, Nanotechnology, 19, 175704 (2008).
36. T. Suga, T. Itoh, Z. Xu, M. Tomita, and A. Yamauchi, Proc. 52nd Electronic Components and Technology Conference, pp. 105 (2002).
37. R. G. Reifenberger, J. Appl. Phys., 106, 104308 (2009).
38. H. Radhakrishnan, S. D. Mesarovic, A. Qiu, and D. F. Bahr, J. Mech. Phys. Solids, 72, 144 (2014).
39. L. Lattanzi, L. De Nardo, J. R. Raney, and C. Daraio, Advanced Engineering Materials, 16, 1026 (2014).
40. H. Radhakrishnan, S. D. Mesarovic, A. Qiu, and D. F. Bahr, International Journal of Solids and Structures, 50, 2224 (2013).
41. A. Qu and S. F. Bahr, Carbon, 55, 335 (2013).
42. S. Pathak, N. Mohan, E. Decolvenaere, A. Needleman, M. Bedewy, A. J. Hart, and J. R. Greer, ACS Nano, 7, 8593 (2013).