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Carbon Nanotube Micro-Contactors on Ohmic Substrates for On-chip Microelectromechanical Probing Applications at Wafer Level

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Abstract:

CNTs can have the ability to act as compliant small-scale springs or as shock resistance micro-contactors. This work investigates the performance of vertically-aligned CNTs (VA-CNTs) as micro-contactors in electromechanical testing applications for testing at wafer-level chip-scale-packaging (WLCSP) and wafer-level-packaging (WLP). Fabricated on ohmic substrates, 500- μm -tall CNT-metal composite contact structures are electromechanically characterized. The probe design and architecture are scalable, allowing for the assembly of thousands of probes in short manufacturing times, with easy pitch control. The effect of the metallization morphology and thickness on the compliance and electromechanical response of the metal-CNT composite contacts is discussed. Pd-metallized CNT contactors show up to 25 μm of compliance, with contact resistance as low as 460 m Ω (3.6 k $\Omega/\mu\text{m}$) and network resistivity of $1.8 \times 10^{-5} \Omega \text{ cm}$, after 2500 touchdowns, with 50 μm of over-travel, displaying reproducible and repeatable contacts with less than 5% contact resistance degradation. Failure mechanisms are studied in-situ and after cyclic testing show that, for top cap and sides metalized contacts, the CNT-metal shell provides stiffness to the probe structure in the elastic region, whilst reducing the contact resistance. The stable low resistance achieved, the high repeatability and endurance of the manufactured probes make CNT micro-contacts a viable candidate for WLP and WLCSP testing.

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1. Introduction:

Applications of electromechanical probing for semiconductor packaging testing require smaller pitches, reliable and reproducible manufacturing and lower electrical contact resistances. Current electromechanical testing probes, for instance microelectromechanical (MEMS) based vertical cantilever probes, have fundamental drawbacks in terms of the shortest pitch that can be achieved, without compromising repeatability, elastic properties, cost and efficiency. However, there is still a commercial need to reduce the pitch of electromechanical probes for testing complex semiconductor structures at wafer packaging level.

Certain electrical and mechanical properties of vertically-aligned carbon nanotubes (VACNTs), such as ballistic electron transport at micron scale¹, very high current-carrying capacities², high elastic modulus³ and excellent mechanical resilience⁴, can be the solution for a new generation of electrical components, ranging from vertical probing structures to electromagnetic interconnects. A typical probe structure, whether it is a cantilever⁵, vertical micro-spring⁶ or MEMS type⁷, is required to be towards millimetric scale in length and to be assembled in to probe cards or insulators as interposer arrays, whilst providing low contact resistances ($<100 \text{ m}\Omega$), with good over-travel (up to $50 \text{ }\mu\text{m}$)^{8,9}. Therefore, high-yield, extra-long ($>300 \text{ }\mu\text{m}$) and high-quality VACNT forests are needed. However, for a probe cross-sectional area of $200 \times 200 \text{ }\mu\text{m}$, up to 10^7 individual CNTs can be grown within, which could result in a $0.6 \text{ m}\Omega$ contact resistance when pure ballistic conduction and perfect metal-CNT contact are achieved (assuming each MWCNT pose a quantum conductance of $6.45(\text{k}\Omega)^{-1}$)¹⁰. The challenge is to connect all these CNTs at the same time to the tested contact and achieve a low contact resistance. In literature, most research studies have focused more on obtaining composite structures¹¹ by means of dispersing CNTs in an insulating, elastic polymeric matrix, to form conductive nanocomposites

for use as sensors and actuators. However, in this process, the CNTs are randomly aligned and the conductivity relies on low CNT to CNT contact resistance (it is typically 100 – 1000 times higher than the resistance of an individual CNT¹²), restricting possible applications, whilst alignment together with good dispersion within the matrix are challenging parameters to control.^{13–16} Utilization of VACNT-based structures as electrically-conductive, compliant electrical connections has been investigated by a number of studies.^{17–20} Yunus et al.²⁰ demonstrated the relationship between contact resistance and contact force on Au-coated CNT forest surfaces, under ultra-low force conditions ($<1\text{mN}$), and reported contact resistances below 1Ω . However, in this study, the CNT lengths were below $40\mu\text{m}$ and the applied forces were too low for any potential probing applications ($<1\text{mN}$). Yaglioglu et al.¹⁸ showed that Au-metallized CNT-based probe structures can achieve good compliances (as described in the semiconductor testing industry the elastic tolerance range over which the contact can be deformed without mechanical damage or contact resistance variation) of up to $10\mu\text{m}$ under cyclic loading, with contact resistances as low as 1.5Ω (approximately one order of magnitude higher than industry requirements) at $50\mu\text{m}$ over-travel. A further decrease in the contact resistance was achieved by using a thicker metal coating, however this came at the expense of reduced compliance.¹⁸ Additionally, these CNT structures were grown on insulating diffusion barrier layers, such as SiO_2 or Al_2O_3 , which prevents the formation of ohmic contacts between the CNT forest and the substrate. Therefore a transfer process is required; however this results in lower yields and layout restrictions.^{17,21} Ultimately the potential benefit of integrating VACNTs in electromechanical micro-probing applications relies on understanding their electrical contact repeatability and mechanical stability.

We propose a design and an architecture with a scalable approach, allowing for the assembly of thousands of micro-contacts, fabricated directly on electrically conductive substrates in short manufacturing times, with easy and precise pitch control. These contacts could facilitate testing Si at wafer level where compliant, small pitch ($< 200 \mu\text{m}$), low contact resistant, high aspect ratio probe structures are required.

2. Materials and Methods:

2.1. CNT Synthesis

In order for as-grown CNTs on Si to be considered for contacting technology, high structural quality VACNTs are grown at low process temperatures (below $<450 \text{ }^{\circ}\text{C}$), under CMOS compatible conditions.^{22,23} The main deposition method for VACNTs has been catalytic chemical vapour deposition (CCVD): a thin film catalyst is partially melted to form nano-islands, acting as seeds for the CNTs to nucleate and grow vertically, without the need for applying an electric field. The tip growth mechanism leads to the formation of CNT forests, with good vertical alignment. However, the elevated process temperatures limit the choice of substrate, particularly when several thin substrate layers, with different thermal expansion coefficients are required.^{24,25} Si requires a diffusion barrier layer between the catalyst and the substrate to prevent silicide formation^{26,27}, and any flexible plastic substrate cannot withstand the severe conditions, leaving mostly Si with insulating layers or ceramic materials as the choice of substrate. A number of groups have demonstrated CNT growth on conducting layers at lower growth temperatures, however the CNT quality, length ($> 300 \mu\text{m}$) and the growth rates ($<200 \text{ nm/s}$) achieved are not always feasible for potential probing application.^{28–31} In this work, we employ a photo-thermal chemical vapour deposition (PTCVD) method in which the catalyst is selectively heated by high-power optical sources (**Figure 1a**), whilst the bulk of the substrate is maintained

at much lower temperatures by water cooling the sample during the anneal and growth stages. Combining this low temperature growth method with conducting diffusion barrier layers enables us to fabricate devices onto conductive substrates, which are kept at temperatures (Figure 1b) that are compatible with CMOS manufacturing processes.^{17,24,25,32,33}

Figure 1. (a) A schematic of PTCVD setup. Thermal heat required for growth is delivered from the top as optical energy by 8 high-intensity infra-red (IR) lamps. Lamps are isolated from the chamber by a 3-mm thick quartz glass. Sample is placed on a water-cooled chuck. Substrate temperature is measured by a pyrometer from the bottom whereas the catalyst temperature is measured using a K-type thermocouple by simply contacting the catalyst surface. (MgO insulated, stainless steel 1 mm diameter). (b) is a typical temperature trend inside the PTCVD chamber. It shows the three stages of deposition; annealing, growth and cool-off. ΔT is the temperature gradient (>300 °C) between the substrate and the catalyst surface due to the design of PTCVD system. Inset is a schematic of the device layer structure for growth. As a barrier layer; SiO₂, Al₂O₃ and TiN can be used. (c-e) Atomic force microscopy (AFM) images of the catalyst annealed at around 350 °C at 10 Torr under 100 sccm H₂ for c) 5 min, d) 10 min and e) 15 min respectively. It is observed that as the annealing time increased the catalyst nano-island particle size increased. This directly affects the as-grown CNT diameter size. (f-k) The Gaussian fitted diameter distribution of the Fe catalyst nanoparticles annealed for f) 5 min, g) 10 min and h) 15 min respectively. Mean diameter, standard deviation, and FWHM of Gaussian curves as a function of catalyst annealing time.

The process temperature was controlled by a digital thermal energy controller (Eurotherm) to adjust the optical energy output. In the PTCVD system (**Figure 1a**), there are eight 1 kW infrared (IR) lamps. Corresponding temperatures of the substrate and the catalyst are measured by a pyrometer and a K-type thermocouple (MgO insulated, stainless steel, 1 mm diameter). **Figure 1b** shows the temperature gradient achieved during a CNT deposition on Si substrate with different thermal/diffusion barrier layers. On a typical growth run, the growth front (catalyst) temperature is kept below 750 °C, whereas the substrate is kept around 400 °C due to continuous water cooling of the substrate and using a thermal barrier layer.^{24,25,32,34}

CNT deposition is carried out on n-type <100> Si substrates. The parameters are chosen to yield extra-long CNT forests (>300 µm) with high growth rates (>500 nm/s). This is achieved by obtaining high process pressures combined with high growth temperatures. A 100 nm thick layer of TiN is sputtered onto a full wafer, followed by e-beam evaporation of an 8 nm thick Al layer and then a 3 nm thick Fe layer. A schematic of a typical substrate structure is shown in **Figure 1b-inset**. TiN is employed as the ohmic contact layer which also acts as thermal and diffusion barrier layer during annealing and growth in PTCVD.^{24,25,32} Al is deposited as a co-catalyst layer to prevent the catalyst from coalescence, increasing the CNT areal density and reducing the CNT diameter.³⁵ C₂H₂ /H₂ gas ratio is maintained at 20 % (25 sccm C₂H₂: 100 sccm H₂) at 10 Torr during the growth stage. Catalyst annealing time varied between 5-15 min and growth was performed for 15 min.

2.2. CNT Density and Diameter Calculations:

The catalyst nanoparticle size distribution is studied using a NT-MDT Solver NEXT atomic force microscope (AFM) equipped with Smena2 and S7 scanners (92.1 x 92.1 µm and 5 x 5 µm maximum scanning area, respectively). All measurements are conducted at ambient conditions

using a high resolution NSG01 Si cantilever in tapping mode. The amplitude set-point is kept high (0.7 nA) to achieve a “light” tapping mode with a 0.25 Hz scanning frequency to increase the resolution. To calculate the catalyst nanoparticle size, both the trace and the retrace signals are used. A minimum of three separate scans are recorded for each annealing temperature condition. The AFM data is analysed with SPM software Gwyddion v2.51. The average nanoparticle diameters are calculated using the image analysis software ImageJ 2.0 with a bandpass filter to increase the accuracy of particle size measurements.

An area density of CNTs is calculated for a 5 cm x 5 cm CNT forest sample (prepared with an identical catalyst deposition and CNT growth recipe that is also used for CNT probe samples, see Figure S1) based on the weight gain method.³⁶ This method is useful as it considers both the number of walls and the length of the CNTs. The CNT diameter is estimated by calculating the annealed catalyst diameter via AFM (**Figure 1 (c-k)**) and sampling the as-grown scanning transmission electron microscopy (STEM) data, (see supplementary info for density calculation details). The average calculated annealed catalyst diameters are 5.93 ± 2.74 (**Figure 1 (c and f)**), 7.51 ± 3.38 (**Figure 1 (d and g)**) and 10.53 ± 4.1 (**Figure 1 (e and h)**) for 5, 10 and 15 min annealed samples respectively. Finally, the average diameter, standard deviation and the full width at half maximum (FWHM) as a function of annealing time are summarized in **Figure 1k**. FWHM is important for catalyst nanoisland diameter calculations to quantify the scatter of diameters around the mean particle diameter. The FWHM of the corresponding annealing time determines how much the catalyst diameter deviates from the average, where a large FWHM attributed to larger errors with catalyst nanoisland diameter calculations. The calculated FWHMs are 7.6, 9.4, and 11.4nm for 5, 10 and 15 min annealed catalysts, respectively. Hofmann et al.³⁷ and other studies³⁸ previously reported that smaller diameter catalyst islands

result in the deposition of smaller diameter CNTs. Therefore, we used 5 min annealing to perform the CNT growth to increase the CNT areal density.

The calculated average areal CNT density deposited with the 5 min annealed catalyst is $1 \times 10^{10} \text{ cm}^{-2}$. This value is comparable with other high density CNT studies reported by Yaglioglu et al.²¹ ($1.5 \times 10^{10} \text{ cm}^{-2}$) and Ahmad et al.²⁴ ($2 \times 10^{10} \text{ cm}^{-2}$) and Gopee et al.¹⁷ (10^{10} cm^{-2}). Therefore, the estimated number of CNTs within a $200 \times 200 \text{ }\mu\text{m}$ cross sectional area of a CNT probe is 4×10^6 .

The overall electrical and mechanical performance of the nanotubes is linked to their quality, which can be assessed using Raman spectroscopy.^{39–41} The D/G (I_D/I_G) band intensity ratio in the Raman spectra is widely used as an indication of sample quality for carbon-based materials.^{42,43} Raman spectra, acquired from different positions along the length of as-grown CNT probes using a 532 nm (2.41 eV) green laser, are shown in Figure S2a and b (see supplementary information for details of Raman spectroscopy characterization. First, as the CNT length increases, the I_D/I_G ratio decreases, indicating an increase in the quality of the CNTs during growth. For a given set of gas flow parameters and catalyst dimensions, the quality typically varies with temperature. Therefore, the quality improvement during growth indicates a temperature increase at the growth front, probably due to the excellent black body radiative properties of CNT. This recovers more of the thermal energy towards the growth front, rather than its removal through the substrate and the high-pressure gas flow.^{24,32} Additionally, when the acetylene gas line is cut off, the optical head is kept on for an extra minute, this could have prevented the formation of an amorphous carbon layer at the tips of the probes. Secondly, the radial breathing mode (RBM) signal of the as grown CNTs are measured by 532 nm and 738 nm lasers and then fitted with Lorentzian functions to measure the intensities and peak positions (see Figure S2 c-d). RBM peaks are

observed only for single-wall (SWCNTs) or double-wall carbon nanotubes (DWCNTs)⁴² and the position and intensities are indications of different type of CNTs with frequencies between 120 and 350 cm^{-1} . The frequency of the “breathing” can be related to the diameter of the nanotubes, however this applies to a narrow range of SWCNT⁴¹ diameter (0.7 – 2 nm). We observe some RBM peaks measured by the 738 nm laser however peaks are very broad with low intensities (see Figure S2c) other than one metallic peak at 226 cm^{-1} frequency which could be associated with C_{60} . No RBM peaks are observed for measurements performed by the 514 nm laser (Figure S2d). This suggest that the deposited CNTs are mostly metallic and multiwalled, since the RBM signal from the large diameter tubes is too weak to be observable.^{41,44} This supports the STEM observations. Micro-probing application requires metallic, high quality for low contact resistance^{17,24} and large diameter multi-wall CNTs for improved stiffness.¹⁹ PTCVD growth recipe we use is designed for metallic multi-wall CNTs (MWCNTs) based on the work done by Chen et al.³² and Ahmad et al.²⁴ With the successful deposition mechanism discussed above, the resultant VA-MWCNTs achieved superior lengths (up to 500 μm), high quality ($I_D/I_G < 0.5$) and greater density (10^{10} cm^{-2}).

3. Results and Discussion:

Here we demonstrate lithographically patterned, CNT-metal composite probe structures fabricated on ohmic substrates. We show that the pitch, array layout and the probe geometry can be controlled through selective CNT growth from fixed pre-patterned catalysts via photolithography (**Figure 2(a)**). These column structures can be produced with very short pitches, even of the order of microns, an area where further minimization of current solid metal micro-contactors towards 50 μm is challenging. We also show that an appropriate metallization

layer reduces the overall resistance by one order of magnitude and provides enhanced mechanical resilience to the probe.

Figure 2. (a) Pd (500 nm) top-cap and sides metallized CNT micro-probes on Si with 200 μm pitch with average length of ~ 500 μm . (b) is a scanning electron microscopy (SEM) image of a CNT forest pillar before metallization. Tilt angle is 80° . (c) is a top-cap and sides metallized (500 nm) Pd-CNT probe after cycling testing for 1000 touchdowns at 50 μm showing the plastic deformation retained. Tilt angles are 70° for (b) and 80° for (c).

The average lowest stable contact resistance measured for an as-grown (non-metallized) CNT probe (**Figure 2(b)**) is $5 \pm 0.5 \Omega$ for an array of 5 randomly chosen probes, at 50 μm over-travel. If we assume that all vertical CNTs resistors are connected in parallel, then the resistance of an individual CNT is 20 M Ω . When the resistance is normalised to per micron length compared with other studies in literature with similar scales ($> 100 \mu\text{m}$ CNT length, see Table 1), we report one of the lowest CNT resistance to date. To calculate resistivity, a cross section area should be defined. Since the probe structure is very porous^F, it cannot be considered as a dense solid. It is shown in literature that when an array of CNT forest is densify the resistance decreases sharply since more conduction channels are employed per area.^{45–47} Therefore, nanoscale void volume should be defined and taken into consideration to estimate a “true cross-section” area of a probe. If we assume, one conduction shell per tube (the outer shell) and the average CNT diameter as 8 nm (see supplementary info Table S1) we can then calculate a cross section area of an individual

CNT ($1.25 \times 10^{-13} \text{ cm}^2$) and multiply that by number of CNTs (4×10^6 CNTs) per $200 \times 200 \mu\text{m}$ probe cross section. This enables us to define an approximate “true” cross-sectional area to calculate resistivity value of $2 \times 10^{-4} \Omega \text{ cm}$ for the as grown CNT forest columns. However, this model presumes that the VACNTs are perfectly aligned and in contact. As discussed in the following section, metallizing CNT probe with 500 nm Pd decreases the network resistivity to $1.84 \times 10^{-5} \Omega \text{ cm}$, almost one order smaller than as deposited CNT samples (Table 1). Lower resistivity could be attributed to the good work function matching and better wetting properties of Pd.^{17,48,49}

Table 1. Comparison of as-deposited and metallized CNT probes' resistance and resistivity values to similar studies with comparable CNT lengths.

Reference	Average VACNT length	Resistance [k $\Omega/\mu\text{m}$]	CNT Diameter [nm]	CNT Density	CNT Network Resistivity*
Pd-CNT (500 nm)	500 μm	3.6	~8	10^{10}	$1.8 \times 10^{-5} \Omega \text{ cm}$
Au-CNT (500 nm)	500 μm	12	~8	10^{10}	$6.0 \times 10^{-5} \Omega \text{ cm}$
CNT-only probe	500 μm	40	~8	10^{10}	$2.0 \times 10^{-4} \Omega \text{ cm}$
Yaglioglu ^[21] (Ag epoxy – CNT)	700 μm	43	10	1.5×10^{10}	$6.7 \times 10^{-5} \Omega \text{ cm}$
Gopee ^[17] (Ag- CNT-Ag)	200 μm	6.5	7.3	10^{10}	$3.1 \times 10^{-4} \Omega \text{ cm}$
Yun ^[50]	4 mm	28	~20	-	-
Agrawal ^[51]	100 μm	10,000	40 ± 10	-	-
Zhu ^[52]	210 μm	138,000	~10	-	-

*Note: Resistivity is estimated as “network” resistivity by considering the average individual CNT cross-section area, the number of CNTs per probe cross-section area, CNT length and contact resistance. The shaded area shown are the results of this work.

In this paper, we also discuss electromechanical characterization and modes of failure of metallized $200 \mu\text{m} \times 200 \mu\text{m}$ CNT probes **Figure 2(c)**. We report that metallized CNT probes have a compliance of up to 5% and exhibit a stable electrical contact resistance for up to 60 μm over-travel. Yaglioglu et al.¹⁸ reported a low compliance, of around 1.5%, which could be the result of much thicker metallization layer (1 μm) and a larger CNT diameter, with a lower areal

density. We show that the metallization morphology and the thickness directly affect the electromechanical response. The lowest contact resistance achieved for non-metallized CNT forests is $5 \pm 0.5 \, \Omega$, for a CNT pillar with a $200 \times 200 \, \mu\text{m}$ cross-section area. However, during touchdown, the contact resistance is found to be unstable ($5\text{-}20 \, \Omega$) (see **Figure S3** in supplementary info.). Additionally, the mechanical stiffness is low due to the foam-like, low-density structure⁴, therefore a metallization process is necessary.^{17,18} A workflow of the micro-contact fabrication process is shown in **Figure 3a**, from the patterning of the catalyst to the growth of the CNT. In this study, tap-cap and sides metallized, (250 and 500 nm) Pd-CNT probes (**Figure 3b**) are compared with top-cap only metallized (250 and 500 nm) Au-CNT probes (**Figure 3c**) to study the effect of metallization morphology and thickness on obtaining a stable electrical contact resistance, without compromising the elastic compliance; this is to be competitive with current technologies, such as MEMS cantilever probes or micro-spring probes, which have good elastic compliance ($>20 \, \mu\text{m}$ over-travel).^{5-7,53,54} Pd and Au are typically used in the contacting industry to give good ohmic contacts. Additionally, wetting properties and the thickness of metallization are critical to obtain a stable contact. **Figure 3d** shows a focused ion beam (FIB) cross section of a 500 nm Pd sputtered CNT contact. We observe that the metal does not penetrate the CNT forest for more than $3\text{-}4 \, \mu\text{m}$. As the metal coating gets thicker, it forms a continuous layer and blocks further penetration even though the inner CNT forest is very porous. The resulting structure is a combination of an outer shell of a hybrid CNT-metal (up to $4 \, \mu\text{m}$) and inner highly dense CNT forest, as observed by the SEM image contrast difference in **Figure 3d**. Similar results are reported by other studies, regardless of the thickness of the coating.^{17,18}

Figure 3. (a) Process flow for the fabrication of CNT metal hybrid micro-contactors. Step 1, cleaning the Si substrate; step 2, sputtering the thermal and diffusion barrier layer of 100 nm TiN, followed by the interlayer deposition of 10 nm Al (Step 3) via e-beam evaporation. Step 4, catalyst patterning by photolithography, e-beam evaporation and lift-off; step 5 is the PTCVD growth of CNT columns. Final step (step 6) is divided into two routes; 6a is sputtering providing a more uniform metal coating, 6b directional metallization of the CNT columns via e-beam evaporation. Two routes are followed to investigate the effect of metalization on the compliance of the CNT-metal micro-contactors probes. (b), A Pd metalised CNT probe via sputtering (64 min, 500 nm) covering both the tips and the sides of the CNT pillar. (c), An Au metallized CNT probe via e-beam evaporation (~500 nm) in which the metal layer covers the first 4-5 μm (the tip) of the CNT pillars. (d) A focused ion beam (FIB) cross section of (b), showing the limited penetration of Pd into the CNT structure.

The electromechanical characterization setup of the CNT-metal micro-contact structures is shown in **Figure 4a**. The setup consists of a high-precision, ultra-low load, single-point load cell (Tedeia-Huntleigh 0.3 kg with a load cell amplifier) attached to a motorised z-stage (Thorlabs 300 mm DC Servo Stage with TDC 001 controller, controlled via Kinesis software), a displacement laser (Keyence LK-G) and a source/measure unit. A ~1.5-mm diameter, Au coated, Cu top contact is attached to the load cell. The applied force, displacement, electrical resistance and time are measured simultaneously. Electrical measurements are performed by four-point resistance measurements using an Agilent B2902A. Two wires are attached to the top copper contact and the other two wires are placed on the copper substrate, enabling four-point probe measurements to be performed. The contact resistance measured is a combination of the CNT-probe and the contact resistances at the two ends of the probe.

Three different types of tests are designed: 1) increasing the loading (compression); to observe the mechanical compliance limits and the effect of loading on the electrical contact resistance; 2) cyclic loading, to test the stability and repeatability of contacts; and 3) constant loading conditions to investigate the current-carrying capabilities. For all the tests, 200 μm x 200 μm cross-section area probes with 200 μm pitch are used. For each measurement, only one probe is contacted. Due to the experimental setup and the small pitch, it is only possible to deflect a CNT probe up to 75 μm before contacting adjacent probes. Therefore, for increasing loading (>100 μm over-travel) experiments, adjacent probes to the testing probe are compressed up to 75 μm (see supplementary info Figure S4), to avoid contacting more than one probe.

Figure 4b is a typical compressive loading-unloading curve for a 250 nm Pd-metallized probe together, with a set of optical microscopy *in-situ* images of the probe showing the displacement of the top contact under compression. The CNT-Pd contact (250 nm) is compressed over a distance of 50 μm , with a strain rate of 1 $\mu\text{m/s}$ (slower than cyclic loading). Unloading is performed at a higher rate (10 $\mu\text{m/s}$), to capture the probe recovery. For cyclic loading conditions, the loading-unloading rates are kept identical. Following the initial contact, the probe and the top contact exhibited a “contact settling region” within the first 5 μm over-travel followed by “the elastic region” where the probe retains its structural integrity under compression, without expanding laterally, however the force-displacement curve was not completely linear. This could be due to a couple of reasons. Firstly, A sphere-on-flat-plate Hertzian contact stress model^{55–57} (see supplementary info for details) is fitted to establish the relation between contact area, stress and resistance. The increase in the contact area between the top contact and the CNT-metal probes is not initially linear (see Figure S5), up to 20 μm displacement (over-travel). This could have resulted in an uneven distribution of the initial

contact stress. Additionally, the tip of the CNT-metal probe is not a perfectly smooth surface due to the composite CNT-metal structure which could affect the force response of the probe due to the irregular surface asperities. Further increasing the over-travel results in the initiation of cracks along the edges of the metal-CNT shell, which could be acting as stress concentration zones, and then the crack propagates. This region can be considered as “plastic deformation”. Due to the nature of the structure, it seems probable that the deformation is being accommodated through direct compression and lateral expansion of the metallized walls of the probe and the forest of inner individual CNTs. In this region, the force-displacement curve starts to deviate from linear. The increased area under the force-displacement curve indicates that more work is required to compress the CNTs per micron, even after elastic region. This is typically seen when a material undergoes strain-hardening, and this could be occurring around the metal-CNT shell, as the hybrid structure is stiffer and bears more load. This results in higher strains compared to CNT forests inside the probes, where there is more room for the CNTs to deflect under compression. However, even beyond the elastic compliance limit ($>25\mu\text{m}$), the probe shows further relaxation within the plastic region, which is observed during rapid unloading.

Figure 4. (a) Electromechanical characterization rig setup for testing CNT micro-contacts. Force, electrical contact resistance, displacement and time are simultaneously measured. Single-point, ultra-low-load load cell was attached to a motorised, sequencable z-stage. Displacement is measured via a laser. The alignment between the Au-coated Cu top contact and the CNT probes is carried out by placing two digital microscope cameras in x and y directions. (b) An in-situ observation of a typical loading and unloading of a Pd metallized CNT probe. There are three stages: 1) Initial Elastic Loading up to the compliance limit, 2) as the force displacement is increased, cracks initiate and propagate usually along the corners and then the structure starts to buckle, 3) unloading, as the load is removed the probe relaxes back towards the original position however some of the plastic deformation persists after top contact is removed. Top contact was removed with a much higher rate to observe the probe relaxation more clearly. Inset is a zoomed-out image of the top contact and the CNT probe in contact prior to deflection.

Electromechanical probing applications can demand more aggressive probing tips to penetrate through contaminants, such as thin native oxides or organic adsorbed layers. However, the force applied by the probe to the test material should be balanced to produce good contacts, such that small instabilities do not break the electrical contact, but without plastically deforming the

probes or leaving scrub marks on the test material.^{8,54,58} **Figure 5a** illustrates the electromechanical response of a Pd-CNT probe under increasing compression. Once the top Au contact has made an electrical connection with the CNT probe (this corresponds to the rapid drop in the contact resistance to just below 1000 Ω within the first 5 μm deflection), it is compressed a further 125 μm , at a rate of 1 $\mu\text{m/s}$. It is assumed that there is no contact between the CNTs and the top contact when the contact resistance is above 1000 Ω . The green shade represents the elastic compliance region, followed by plastic deformation. The electrical contact stabilises within the elastic region and remains stable up for up to 60 μm deflection. Higher forces are also required to compress these Pd metallized probes when compared to the corresponding top-cap metallized Au probes (see supplementary info., **Figure S3 (a-b)**). This is because the outer metallic shell of the Pd metallized probes combine with the inner CNT forest to give a greater rigidity to the probe structure compared to the top cap metallized Au probes, where the CNT forest is offering the only resistance to compression. Porosity calculations based on CNT areal density and average CNT diameter described by Futaba et al.⁵⁹ suggest that our CNT forest occupy 2.4% of the total volume of a 200 μm x 200 μm x ~500 μm probe; the rest is empty space, (with 21 nm average spacing between individual tubes) resulting in the porous structure. Therefore, the actual applied forces on each tube are many times higher, causing deformation and buckling. Once the electrical contact is made, all probes show a similar range of over-travel (40–55 μm) for which the contact resistance is low independently of the metallization type. However, only metallizing the tip did not provide extra elastic compliance. Compressing the probes beyond this region results in unstable spikes in the contact resistance. In literature, it's been shown both experimentally and theoretically that, under strain, the electromechanical behaviour of SWCNTs and MWCNTs is different.^{16,60,61} There are two arguments for SWCNTs:

1) Mechanical deformation such as stretching, bending, compression introduces a band gap for both semiconducting and metallic type CNTs, causing a decrease in the conductance^{62,63}; 2) A transition from sp^2 to sp^3 bonding configurations when strained results in a reduction in conductance.^{64,65} It is noted that this transition is localised to the strained region and it is reversible. MWCNTs, however showed an increase in conductance when bent or compressed. This is attributed to the increasing the number of charge carrying channels in contact within a tube and parallel transport through them, causing a significant increase in the conductance.^{20,21,66} When compressed both metallized (**Figure 5a**) and as-grown CNT probes (**Figure S3d**, see supplementary info) show a decrease in the resistance as a common trait, even though the amount of decrease is different. However, under high strains, deformation of the CNTs and collapsing of the adjacent walls cause an increase in the contact resistance. Overall, to ensure good stable contact resistance for the Pd and Au probes, the over-travel should be limited to a maximum of 50 μm .

The highest Young's modulus (35.7 MPa) is obtained for the 500 nm Pd metallized probes, prior to significant plastic (non-recoverable) deformation, whilst the 250 nm top-cap only metallized Au probe had a Young's modulus of 7.6 MPa. Ajayan's group⁴ reported a modulus of 5.85 MPa for a compressed CNT forest film, stating that, compared to low-density flexible foams, nanotube films showed much higher compressive strength. The contact stresses with respect to the applied forces are 5 MPa for Pd and below 1 MPa for Au at 50 μm deflection, suggesting low contact stresses compared to MEMS technology.^{54,58} One of the drawbacks of solid, metal-based micro-contactors probes is that the smaller the probe needle gets, the more force they exert per area, causing unwanted damage to micro solder balls or leaving behind scrub marks, as in the case of MEMS cantilever probes.^{67,68} Therefore, CNT-based micro-contact probes' with 'low-

resistance, soft contacting” could be advantageous for probing applications, where low stress forces are required, without compromising the contact resistance.

Figure 5. (a) Electromechanical response of 250 nm Pd metallized CNT micro probes ($200\ \mu\text{m} \times 200\ \mu\text{m}$) under increasing loading conditions for up to 125 μm deflection. After initial contact was established, the probes were compressed 125 μm with a rate of 2.5 $\mu\text{m/s}$. Sample showed a higher resilience to compression within the first 20 μm over-travel with stable, whilst maintaining below 1 Ω contact resistances up to 60 μm over-travel. (b) Cyclic loading electromechanical test of the same sample. Each peak represents a single touchdown. 1000 cycles were performed for each sample with 50 μm over-travel after contact. Force unit is gram-force. Contact resistance remained stable for all touchdowns. (c) Current-voltage characteristics of $200\ \mu\text{m} \times 200\ \mu\text{m}$ cross section area CNT probes with different metallization layers and thicknesses. Probes are deflected 20 μm before the measurements and remained constant during the measurements.

Current micro-contacting technology expects probes to perform at least 100,000 stable touchdowns before they are replaced.^{58,69} Consequently, the mechanical and electrical behaviour of the probes under cyclic loading need to be studied. The cyclic loading results of Pd-metallized CNT probes are shown in **Figure 5b**. As discussed in the previous section (**Figure 5a**), the contact resistance reaches a low and stable value within the elastic compliance region (approx. 20 μm over-travel); however, to characterise the limitations of the probes, the over-travel is kept to 50 μm for each touchdown. In **Figure 5a**, we show that the contact resistance is stable at 50

μm over-travel, with Pd providing lower contact resistance ($< 1 \Omega/\text{probe}$) than Au ($< 3 \Omega/\text{probe}$), regardless of metallization thickness. The higher contact resistance for Au could be due to the other factors, such as the work function mismatch and poor wetting between the metal and the CNT column.^{17,48,49} Matsuda et al.⁴⁸ showed that, for an end-to-end metal-CNT-metal type of structure, Pd had a lower contact resistance than Au. Likewise, Lim et al.⁴⁹ argued that wetting of carbon by transition metals was directly related to the number of unoccupied d orbitals and showed that Pd provided better wetting of CNTs compared to Au. Similar results are reported in Gopee et al.'s interconnect study.¹⁷ Additionally, the forces measured are significantly higher for Pd metallized probes compared to Au metallized. This could be the result of the deposition morphology as discussed in previous section. The force curve recorded for the first couple of touchdowns shows 10-15% higher resistive forces before it stabilises, regardless of the probe metallization type or the metal thickness. This is due to the morphology of the contacting surfaces inducing small plastic deformations (e.g. indents, scratches) in these initial contacts. This is not observed when repeating these cyclic loading tests with smaller over-travel values of up to $25 \mu\text{m}$ (depending on the metal coating morphology and thickness), indicating that the lower forces induced in the loading cycle are not sufficient to plastically deform the contacting surfaces.

Additionally, microcontacts are expected to have high continuous current carrying capacities ($>1 \text{ A}$) at operating temperature.^{58,69} **Figure 5c** shows the current-voltage characteristics of the CNT probes acquired at room temperature, under $20 \mu\text{m}$ deflection (stable contact resistance region). We observe that the current increased linearly indicating ohmic microprobes (with current density per CNT-metal probe as high as $2.5 \times 10^6 \text{ A cm}^{-2}$) and that the probes did not degrade even for currents as high as 1 A , suggesting that these probes could be suitable for applications

where high continuous current carrying capacities are required. For example, the current rating of a Cu wire with the same cross-section (0.04 mm^2 gauge AWG31) has a maximum power transmission current of 0.01A. We have safely tested our metallized wires to 1A which, given the very small thickness of the metal layer, shows that the ampacity is due to CNT conduction. Furthermore, due to the top-down nature of the metallisation deposition, it is likely that the metal cap is thinning significantly towards the bottom of the CNT contact, which would affect the current-carrying capacity if just the metal were responsible for conduction.

Figure 6. Evaluation of reproducibility and repeatability of contacts of $200 \times 200 \text{ } \mu\text{m}$ cross-sectional area CNT-metal probes. 5 random probes were chosen and tested for 2500 cycles at $50 \text{ } \mu\text{m}$ over-travel. Only every 15th data point is displayed in this graph to be able show the variance more clearly.

In **Figure 6**, we trace the evolution of the contact resistance over 2500 touchdowns. For each metallization, we select 5 random probes and contact them for 2500 cycles, with $50 \text{ } \mu\text{m}$ over-travel. The traces in Figure 6 represents the average over the 5 randomly-selected probes. Each line is the average over five independent traces, over 5 different probes, respectively. 500 nm

top-cap and sides metallized Pd CNT probes had the lowest contact resistances, as low as $0.44 \pm 0.01 \Omega$ within the first 50 touchdowns and $0.46 \pm 0.01 \Omega$ ($3.68 \text{ k}\Omega/\mu\text{m}$) in the last 50 touchdowns, whereas 250 nm Pd shows $0.69 \pm 0.03 \Omega$ ($3.68 \text{ k}\Omega/\mu\text{m}$) initial and $0.73 \pm 0.02 \Omega$ final resistance after 2500 cycles. (See supplementary information for the distribution of the contact resistances for each probe after 2500 touchdowns). Top-cap only metallized Au samples' contact resistance results vary more compared to Pd. 500 nm Au metallized probes had an initial contact resistance of $1.46 \pm 0.03 \Omega$ and a final one of $1.52 \pm 0.04 \Omega$ ($12.16 \text{ k}\Omega/\mu\text{m}$), whilst 250 nm Au probes initial and final contact resistances increase from $2.62 \pm 0.01 \Omega$ to $2.72 \pm 0.04 \Omega$ ($21.76 \text{ k}\Omega/\mu\text{m}$). Overall, the increase in the contact resistance does not exceed 5% for Au samples, and 4% for Pd samples after 2500 touchdowns. Higher degradation in the contact resistance for Au could be linked to the poorer contact interface between Au and CNTs.^{17,70} If we calculate a resistivity value based on average cross-section area of an individual CNT and estimated number of CNTs per probe area, the lowest metal-CNT array network resistivity calculated is $\sim 1.8 \times 10^{-5} \Omega \text{ cm}$ for the 500 nm Pd-metallized CNT probes. This value is an order of magnitude smaller than Gopee et al.'s¹⁷ interconnect ($3.1 \times 10^{-4} \Omega \text{ cm}$), Ahmad et al.'s²⁴ metallized CNT via ($8.37 \times 10^{-5} \Omega \text{ cm}$) and Yaglioglu et al.'s²¹ probe ($6.7 \times 10^{-5} \Omega \text{ cm}$).

Figure 7. (a-h) Top-cap and sides metallized (500 nm) Pd-CNT probes after cycling testing for (a) 1000 touchdowns, (e) 2500 touchdowns. After 1000 touchdowns, lateral expansion (c) and tearing along the edge of the probe (b) of the side walls as well as micro-cracks ($<1\ \mu\text{m}$) within the body of the probe (d) observed after 1000 touchdowns. Further touchdowns resulted in enlargement of the micro-cracks (f) and further lateral expansion of the sidewalls causing detachments of the inner shell (g). (h) is an example of “branching” of CNTs across a large crack. (k-n) Top-cap metallized (500nm) Au-CNT probes after cyclic and increasing loading, (k) is after 1000 touchdowns with $50\ \mu\text{m}$ overdrive after contact, (l) 2500 touchdowns. (m) is a zoomed in image, showing the buckling effect under low over-travel ($< 50\ \mu\text{m}$). (n) is a $125\ \mu\text{m}$ over-travelled probe edge showing complete buckling without lateral expansion. It should be noted here that there is no apparent damage/deformation to the surface of the probe. Different probes were used for each test. Tilt angle is 80°

Figure 7 shows the SEM images of the Pd and Au metallized CNT contacts after 1000 and 2500 touchdowns, in the plastic region ($50\ \mu\text{m}$ over-travel) to investigate limitations. The deformation induced after cyclic loading showed splitting of strands of the CNT-metal outer shell-wall along the edge of the probe and lateral expansion of the CNT-metal shell (Figure 7 (b-g)). It is observed that the CNT forest within the probe remain intact (Figure 7 (c and g)), which could explain the stable contact resistance beyond elastic region up to $60\ \mu\text{m}$. Additionally, we observed branching of CNTs across large cracks. Au metallized probes however, (Figure 7 (k-n)) showed buckling without lateral expansion (Figure 7 (m,n)); this is probably due a more porous internal structure of the probe. It should be noted here that the tip of the probes did not show any apparent

deformation/damage, we believe this is because of the presence of Au metal at the tip which provided rigidity, while the rest of the body is compressed and buckled. Considering (i) the deformation observed in the SEM micrographs and (ii) the good low contact resistance obtained for shorter over-travel distances, the over-travel could be reduced below 50 μm (to 25-30 μm) and still a low contact resistance can be achieved, but with reduced plastic deformation and increased durability/longer lifetimes of the probes.

4. Conclusion:

In summary, we have shown that VACNT-metal composite compliant micro-probe structures can be a realistic substitute for current micro-contacting technologies. The process does not require transfer of probes on to conductive substrates and is highly scalable, allowing for the patterns of fabrication of thousands of probes, with precise pitch control. The fabricated micro-contacts have a compliance of up to 25 μm , with contact resistances as low as 0.46 Ω (3.6 $\text{k}\Omega/\mu\text{m}$, CNT array resistivity of $1.8 \times 10^{-5} \Omega \text{ cm}$) for a 200 x 200 μm cross section area, with a 200 μm pitch revealing one of the lowest values reported to date across comparable geometries. They are tested successfully for 2500 touchdowns, across 5 random probes, at 50 μm over-travel. The electrical contacts are repeatable and reproducible. It is observed that the metallization morphology and thickness affect directly the electromechanical properties of the CNT probes. Cyclic and compression electromechanical tests showed that only metallizing the tip of the CNT forests with Au did not provide extra compliance; the structure proved to be too porous and the elastic modulus is low (7.6 MPa). Top-cap and sides metallized Pd-CNT probes provided good stable contacts, however under increased strains they exhibited lateral expansion of the probe shell walls. As a result, of cracks induced along the edges. We believe CNT-based-metal hybrid probes have comparable to solid metal micro contactors with easy scalable fabrication and

precise pitch control, exhibiting greater potential for their utilization in miniaturized contact technologies. We believe these hybrid structures may also be used as shock absorbent interconnects, conductive micro-springs and compliant thermally-stable interfaces. In future, the research should be furthered by increasing the strength/stiffness of the probes and by better understanding the addressability of individual probes, as well as the planarization effect (perfect planarization assumes that all probes make simultaneous contact with the device under test) of an array, tackling the current challenges associated with contacting applications and allowing to test micro/nano Si devices at wafer level.

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