New Insights on the ESD Behavior and Failure Mechanism of Multi Wall CNTs

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***Abstract*—In this work, for the first time we experimentally determine ESD behavior of individual shells of both single and bundles of MWCNTs. Distinct electrothermal transport, under ESD conditions, through inner and outer shells of MWCNT is explored. ESD time scale current annealing behavior of outer and inner shells was discovered, which is unique to MWCNTs. Shells – by – shell failure was confirmed to be the universal failure mode of MWCNTs. Failure behaviors of suspended and collapsed (tubes resting on dielectric surface) tubes in single and bundled configuration are discussed.**

***Index Terms*--Annealing, Carbon nanotubes, Electric breakdown, Electrostatic discharges, Electrothermal effects**

I. INTRODUCTION

High current carrying capacity and resiliency towards electro-migration have made Multi-Wall Carbon Nanotubes (MWCNTs) a promising contender for future interconnects. Although much has been done on growth, process optimization and modeling of these tubes, the analysis of their reliability under electrical stress and in particular ESD stress is still a crucial and largely unexplored area. Existing literature on ESD reliability of MWCNTs focuses only on single tube configuration [1] [2]. Since electrical and thermal transport strongly depends on thickness, length and method of growth of tubes, therefore, a complete picture of ESD reliability of MWCNTs can be obtained by co-investigation of both single and bundles of tubes in different configurations, which is missing in the existing literature. Moreover, ESD behavior of individual shells of MWCNTs was never reported before. Understanding of failure of very long tubes for interconnects and very short tubes for vias are also missing in literature.

II. DEVICE UNDER TEST

MWCNTs used in this work were grown by thermal chemical vapor deposition (length = 500nm to >10µm, diameter 50 – 150nm), and uniformly dispersed in N,N-Dimethylformamide using sonication for 30 minutes. Thereafter, CNT suspension was dielectrophoretically deposited [3] across a series of electrode gaps (Fig. 1). Concentration of suspension was tuned to 10µg/ml for bundles of CNTs and 100ng/ml for depositing a single CNT across an electrode gap. Electrodes, with gap size ranging from 250nm to 26µm, were lithographically patterned on Si/SiO_2 substrate, followed by Cr/Pd (5/50nm) evaporation and lift-off in acetone. Post deposition dies were cleaned in warm DI water (90°C), followed by solvent bath and dehydration bake at 200°C (15 minutes each). Such a deposition technique ensured that (i) only the outermost shell (henceforth, referred as the 1st shell and its breakdown as 1st breakdown) contacts the metal pads, and hence paved the way to look into the effect of ESD stress on individual shells and (ii) both suspended and collapsed tubes are obtained (depending on aspect ratio and electrode gap). The latter feature gave the qualitative insight into the role of surface in mitigating ESD stress. ESD behavior of individual shells was captured by precise and controlled TLP measurements in recursive fashion. All TLP measurements were performed with 1ns rise time. Spot measurements post TLP pulses were done at 0.5V. Given that a typical 50 nm thick MWCNT gives around 1 mA of current under DC condition, it is worth highlighting that the TLP setup was modified for low current sensing. For precise low current TLP measurements a state-of-the-art TLP tester from HPPI was complemented with a high resolution (1mV/div with 8 bit sampling) mixed-domain oscilloscope and a highly sensitive current sensor with detection capability in the range of few 10s of micro-amps and sensitivity of 5mV/mA. It is also important to mention that this work targets fundamental behavior of CNTs under ESD conditions, therefore TLP pulses with different pulse widths were used for investigations, rather than emulating ESD stress using models like HBM, CDM etc. It is too early to study, for example, HBM behavior of single CNTs. This approach also gives physical insights into the transport behavior of CNT's under ESD conditions, which gives a vital piece of information, as the MWCNTs attain thermal equilibrium in few tens of nano-seconds.

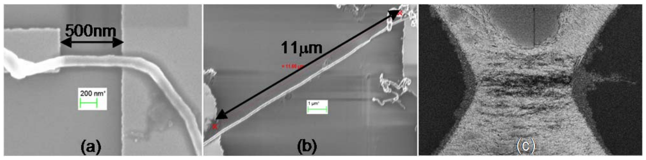

Fig. 1: SEM image of dielectrophoretically deposited undamaged MWCNTs (a) Suspended tube with 500nm length; (b) Collapsed (resting over the dielectric surface) tube with 11µm length and (c) Bundle of collapsed MWCNTs with 26µm length.

III. UNIVERSAL SHELL-BY-SHELL FAILURE AND CURRENT ANNEAL

DC behavior of a typical side-contacted MWCNT shows a linear response in the low-voltage region, (conduction through outermost shell only) and exponential in high-voltage region (conduction through both outer and inner shells). Such a behavior at high voltages causes excessive self-heating and

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results in abrupt and simultaneous breakdown of all the shells. This is triggered at ~600°C and depends strongly on device length and current density [4]. However, during ESD stress, it breaks down into multiple sub-events, each giving information related to distinct shells (Fig. 2). For low voltages, conduction happens along the outermost shell only and current rises linearly due to metallic nature of the tube. However, in few tubes, the behavior changes to exponential. This was earlier explained using enhanced injection attributed to tunneling through high energy sub-band [1]. However, we reveal for the first time in this work that the exponential increase in current at higher TLP voltages is attributed to annealing of contacts because of joule heating (Fig. 2). One should note that a large contact resistance between nanotube and metal contact is often present. This depends on how contacts are made and in case of this work it is attributed to weak chemical bonding between metal and CNT due to large bond length. Joule heating at the interface, as a result of electron – phonon scattering at the CNT – metal interface strengthens the chemical bonds between un-hybridized *p* orbital of MWCNT's outermost shell and the *d* orbital of the metal. This eventually reduces the interface resistance and is depicted as annealing of the contacts in this work.

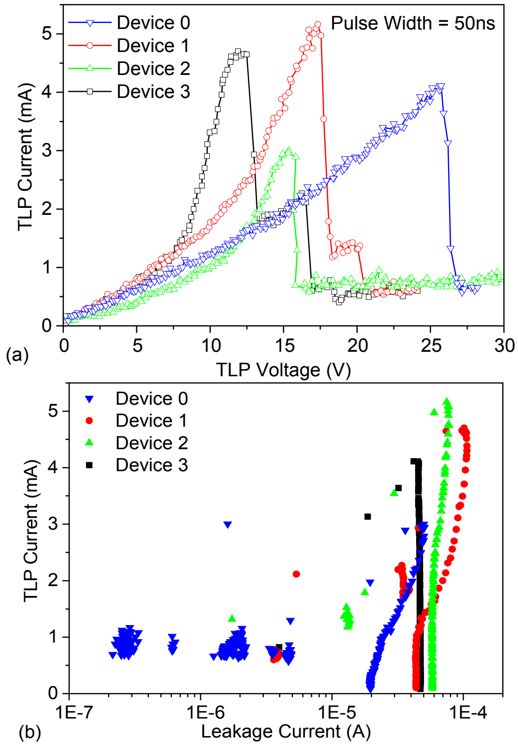

Fig. 2: Measured TLP Characteristics (PW=50ns) of MWCNT deposited between electrodes with spacing = 2μm. Electrical annealing of tubes under ESD stress condition can be observed. Linear I-V behavior can be seen when no current annealing was present; however exponential characteristics can be noticed in the presence of current annealing.

Current annealing is confirmed by spot (low voltage DC) measurements, which depicts increased DC current even at very low voltages. Beyond critical field and current density, population of optical phonons increases with the applied TLP voltage, which gives rise to joule heating sufficient to break the outermost shell. This can be noticed by sharp drop in TLP as well as DC current. However, in most of the cases, current doesn't reduce to open conditions, which depicts presence of parallel conduction paths with higher failure voltages (Fig. 2). This behavior was used and precisely controlled to burn shell after shell to investigate ESD behavior of inner shells. Current annealing at ESD time scales is further confirmed using transient analysis (Fig. 3). Finally, increasing failure voltage of MWCNTs can be noticed from TLP measurements of various devices with length varying from 250nm to >10μm (Fig. 2, Fig. 4 – 9). Moreover, it can be confirmed from measurements summarized here that shell – by – shell failure under ESD condition is a universal phenomenon associated to MWCNTs. Note that the current carrying capacity and failure current of a shell in MWCNT depends on their chirality, defect density and diameter. Current growth and deposition techniques are not matured enough to have a strict experimental control on these parameters. Consequently, the failure current cannot be quantified precisely and the abrupt decrease in current is the only indicator of shell failure. Shell by shell failure of MWCNTs has been discussed in detail in earlier works [1] – [2].

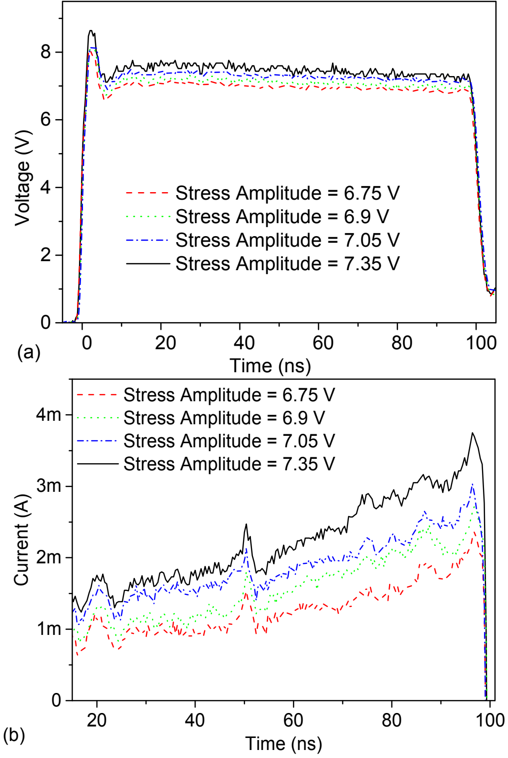

Fig. 3: Transient waveform depicting current annealing in time domain.

IV. CURRENT TRANSPORT THROUGH INNER SHELLS

As explained above, controlled burning of shell after shell is used to investigate ESD behavior of inner shells of MWCNTs (Fig. 4 – 6). Following observation can be drawn from these investigations: (i) Failure current of inner shells is in general lower compared to outer shell, however failure voltage mostly increases (Fig 5); (ii) In some cases, higher failure current of few inner shells was noticed; (iii) Failure voltage nicely scales with tube length (Fig. 5a vs. Fig. 5d); (iv) Outer shells may show linear behavior, however inner shells may independently have exponential behavior with current anneal. This can be attributed to semiconducting nature of 33% shells in a MWCNT; (v) few of the inner tubes may have significantly high conductance (because of metallic nature of the individual inner shells) compared to outer shells (due to semiconducting nature of the outer shells), however only under ESD conditions (Fig. 6). Note that the high voltage ESD pulse enables conduction through inner shells, while the low voltage DC bias results in conduction through outer shells. This is confirmed by spot measurements – measurements depict much higher TLP current, however lower DC current than outer shells and (vi) finally, inner shells may achieve same conductance as outer shells before failure by current annealing at ESD time scales (Fig. 4).

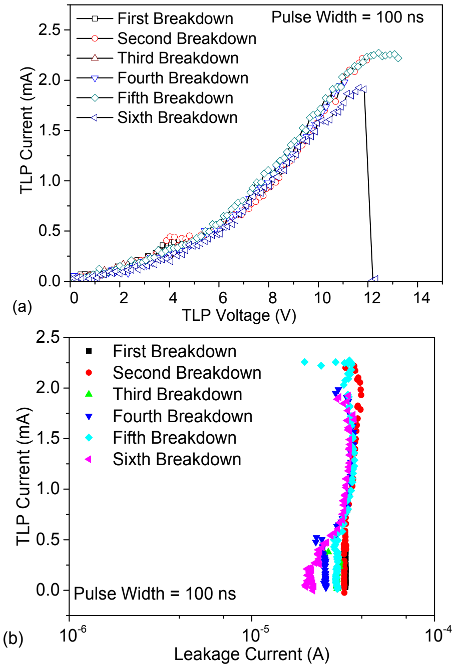

Fig. 4: TLP characteristics of outermost and inner shells of a MWCNT depicting unchanged current conduction through inner and outermost shells even after systematic shell – by – shell failure. However, DC current reduces after each fail. This is attributed to current annealing of inner tubes attributing to same ESD current.

V. CONTACT RESISTANCE LIMITED ESD CURRENT TRANSPORT

Transport properties of MWCNT decide the breakdown voltage and failure current. Electrical transport in short and suspended MWCNTs is ballistic, as a result maximum heating and tube destruction occurs near the interface. During ESD stress, a major fraction of the suspended tube remains devoid of self-heating and as a result only contact resistance puts upper limit on failure current (Fig. 7).

VI. UNIQUE FAILURE BEHAVIOR

Distinct failure behavior was observed in case of suspended and collapsed tubes (Fig. 8 – 10). Following observations were drawn from TLP measurements and failure analysis (failure images are shown in Fig. 10): (i) suspended tubes often show linear or exponential TLP characteristics (no current saturation) with shell burning / destruction close to hot contact pad. Note that suspended tubes are short in length. This can be attributed to ballistic transport through short / suspended tubes, which may heat – up contact pads (because of thermalization of energetic electron in the metal contact). The heat dissipated across contact pads can propagate back to CNT and can damage it close to contacts. (ii) Collapsed tubes show current saturation just before failure.

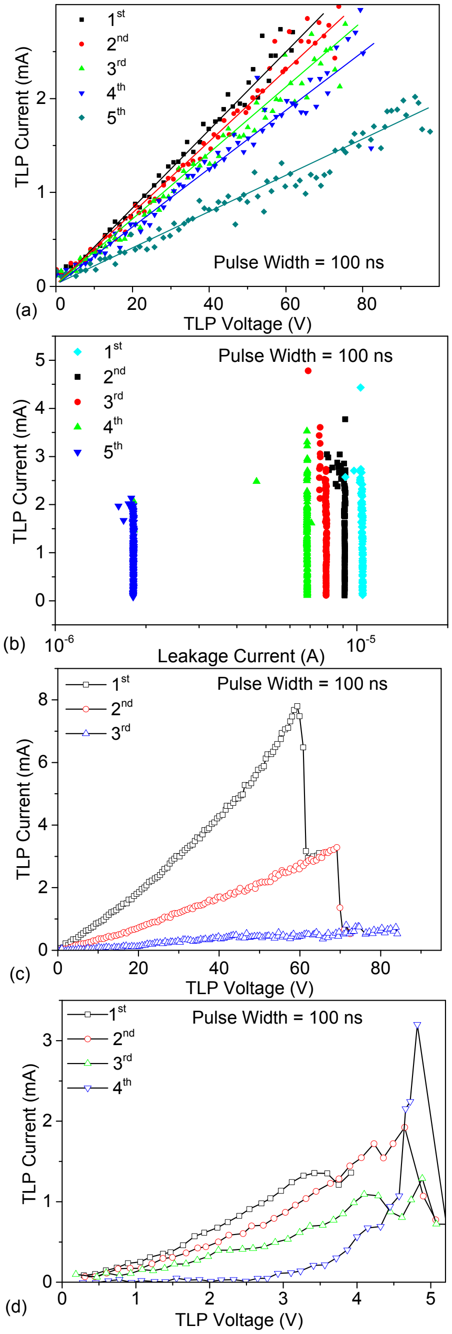

Fig. 5: Measured TLP Characteristics (PW=100ns) of outermost and inner shells of MWCNTs (a & c) bundles deposited over electrodes with spacing = 26μm and (d) single tube deposited over electrodes with spacing = 0.25 – 0.5μm. Three cases were found: (i) Failure current of most of the outer shells remain same with increasing failure voltage, (ii) Failure current and voltage falls with individual shells and (iii) Failure current falls, but failure voltage increases. The on-resistance of the TLP characteristics falls in all the cases. (b) DC current shifts after each fail.

This can be a signature of excess heating, which limits current because of increased phonon population and dominant electron – phonon scattering. These collapsed / longer tubes in general get damaged / burn close to their center. This could be attributed to diffusive transport leading to hot spot formation at the center of the tube. This behavior can accelerate at the center when tubes make contact with dielectric surface because of increased scattering due to surface phonons. (iii) The failure behavior of collapsed tubes however is different in case of bundles. Electromigration of contact metal was observed in a number of samples with MWCNT bundles. Interestingly a melt at the cold pad was also noticed, which depicts significant amount of heat transport through CNTs under ESD condition. Note that the failure behavior of CNT bundles is very different from that of a single tube. This is contrary to what is generally observed in conventional silicon devices or metals, where the linear scaling can relate the physical quantities among up-scaled or down-scaled devices. Although bundling of tubes increases their current handling capabilities, a direct linear extrapolation of the physical quantities and failure mechanism cannot be derived because of the following experimental constraints: (i) number of CNTs in a bundle cannot be precisely controlled with the existing deposition techniques, (ii) current flowing through individual tubes is not the same and depends on various factors like chirality, defect density, tube's diameter and contact resistance, which cannot be directly controlled via the available set of experiment methods. Moreover, the electrical properties of single nanotube are entirely different from that of the bundle. For example, single MWCNT can behave as a ballistic conductor; however the same when bundled behaves like a diffusive conductor.

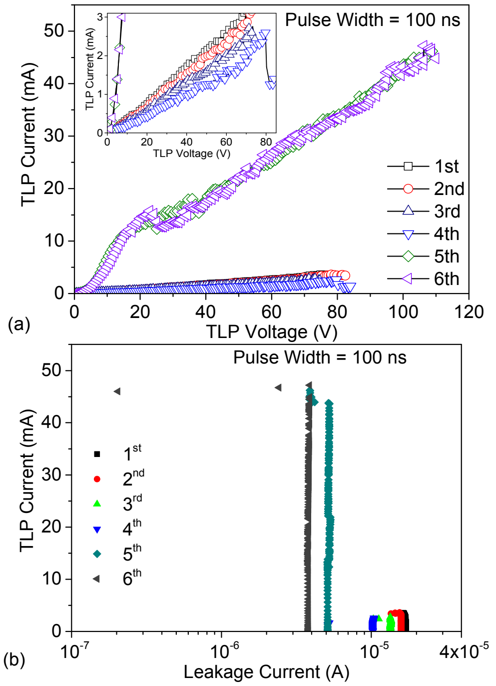

Fig. 6: TLP characteristics of inner and outermost shell of a MWCNT bundle. This depicts extremely high current conduction through innermost shells under ESD conditions, whereas DC current through inner shells remain significantly lower than the current through outer shells like previous observations. Failure voltage of inner shells is consistently higher than outer shells. Zoomed view of (a) is shown in the inset.

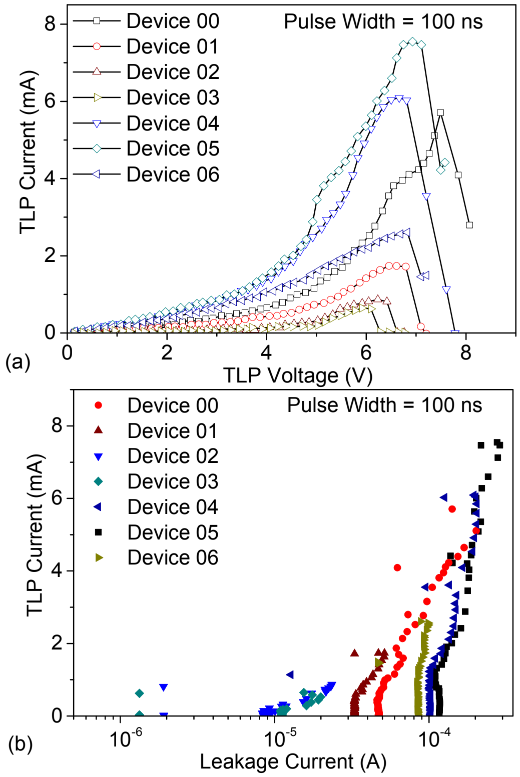

Fig. 7: TLP characteristics of various short length single MWCNTs (0.25 – 0.5µm) investigated depicting strong current anneal and ESD current limited by contact resistance of tubes.

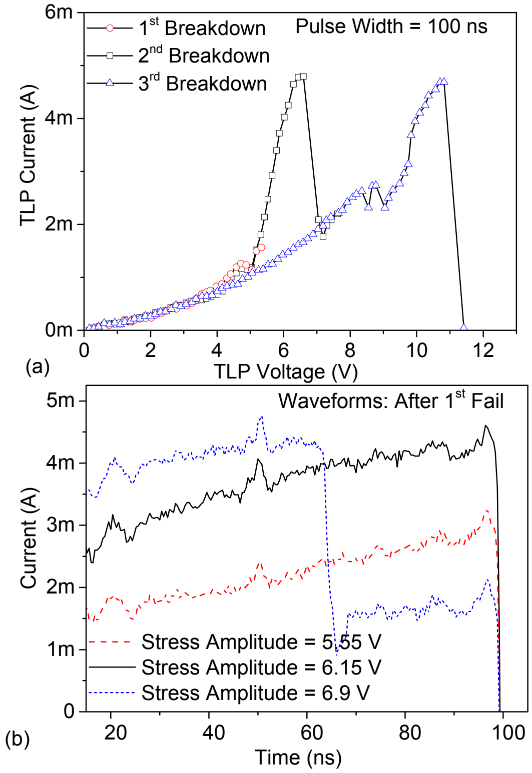

Fig. 8: Unique failure behaviors of single MWCNTs in conjunction with current anneal.

VII. CONCLUSION

ESD behavior of inner and outermost shells of MWCNTs was explored using precise and controlled shell – by – shell burning of MWCNT shells. ESD time scale current annealing of outermost and inner shells was discovered, which is attributed to joule heating and is unique to MWCNTs. Shell – by – shell failure is observed across most of the devices stressed and is confirmed to be the universal failure mode of MWCNTs. Failure behaviors of suspended and collapsed (tubes resting on dielectric surface) tubes are found to be distinct and are related to ballistic vs. diffusive carrier transport through the tubes. Moreover, Electromigration of contact metal was observed in MWCNT bundles, with damage of contacts and CNTs at both hot and cold ends.

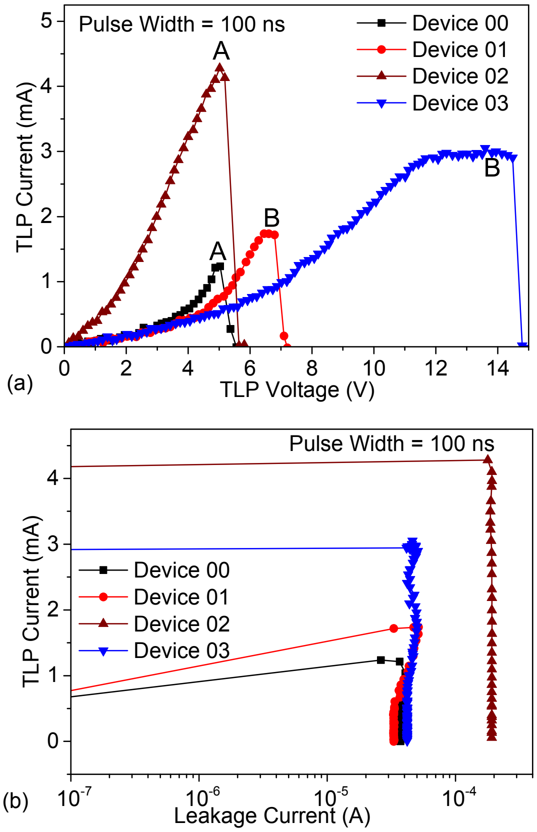

Fig. 9: Unique breakdown characteristics of single MWCNTs depicting: (A) Breakdown without current saturation and (B) breakdown with current saturation.

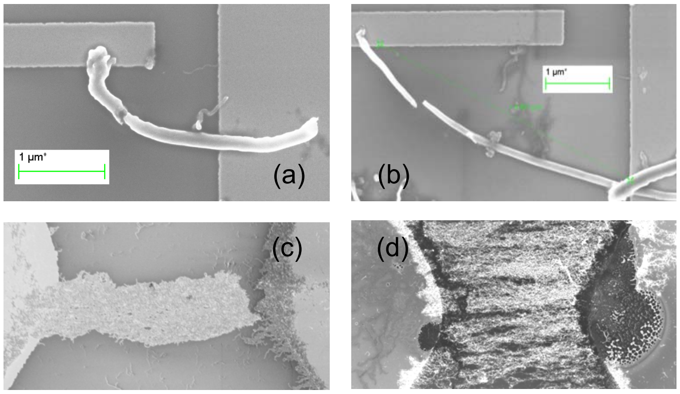

Fig. 10: SEM image of MWCNTs failed under ESD condition. (a& c) are suspended tubes, while (b & d) are collapsed tubes.

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