

Carbon Nanotubes for Interconnects and Switches

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Horizontal Interconnects

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Summary

Wafer level technologies for horizontal interconnects have been evaluated. In the first technology direct horizontal CNT growth between silicon electrodes of various shape have been investigated on the horizontal test vehicle (HTV) made by Intel.

The localisation of catalyst on the edges of the electrodes has been obtained with a PVD catalyst deposition system. The localisation of the catalyst has been achieved by a combination of lift off and ion beam etching performed at 90° incidence. The developed catalyst systems are iron or a stack of aluminium iron. The stack of 10nm aluminium and 2nm of iron is most suitable to grow horizontal CNTs. The achieved density with this technique is close to 10^{11} cm^{-2} CNTs. By using an alcohol dipping technique, the CNT membrane adheres well on the device. A membrane thickness below 100nm has been demonstrated. The contact resistance of the CNTs growing on polysilicon has been measured to be around 10^8 ohm/CNTs . This resistance is at least two orders of magnitude higher than the resistance on vias partly due to the polysilicon nature of the electrode.

In the second technology vertical growth of CNTs is achieved and then the grown structure is flipped in the horizontal direction. A limited amount of work has been done with this technology on modified HTV wafers. Vertical walls of tubes are grown on one electrode then flipped with the alcohol dipping process. The control of the flipping direction is obtained for CNT walls. Without optimisation a density of $9 \cdot 10^{11} \text{ cm}^{-2}$ has been obtained. Other trials have been made with narrow trenches in silicon using via technology. In that case, flipping is much easier and well controlled and the ultimate density can be the density achieved in vias. This last technology is the most promising with the potential to make direct connection between via and lines without adding contact interface.

Table of contents

I. Horizontal CNT growth approach

I.1 Introduction

I.2 Technology developments

I.2.1 Growth Test structures

I.2.2 Process flow

I.2.3 Catalyst Integration

I.2.4 CNT growth

I.2.5 Results on the different electrode structures and density

I.2.6 Alcohol dipping

I.3 Electrical results

I.3.1 CNT growing from one edge

I.3.2 CNT growing from two edges

I.4 Summary

II Vertical growth with flipping approach

II.1 Concept

II.2 Process flow

II.3 Devices

II.4 Flipping technology

II.4.1 Control of flipping direction

II.4.2 Flipping of wall

II.4.3 Flipping of CNTs from via and trenches

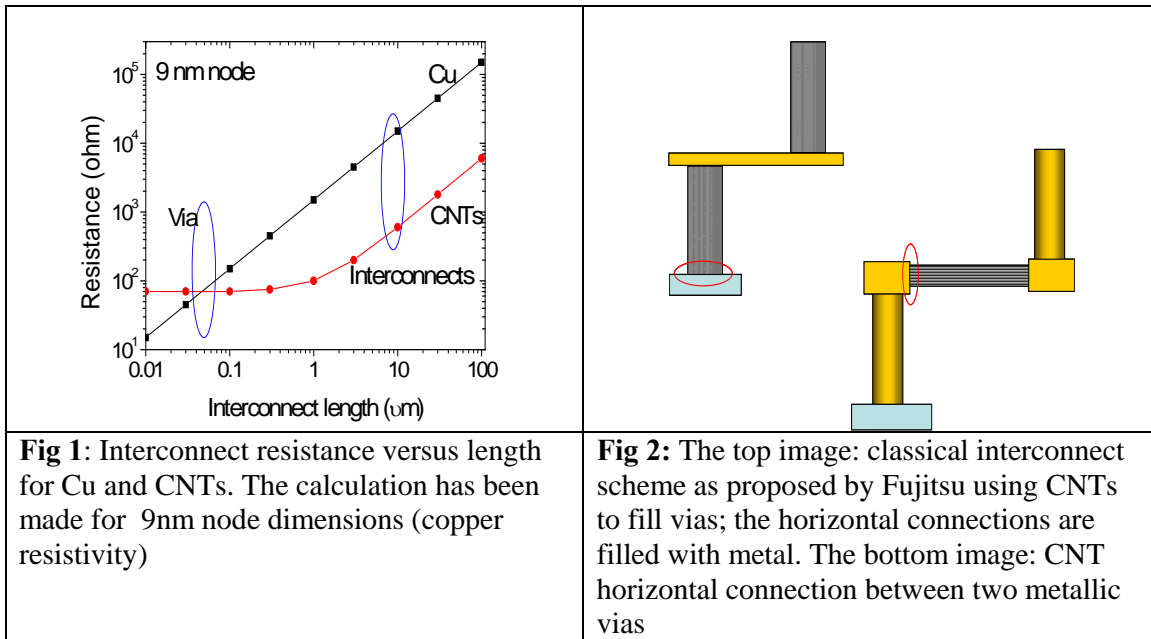
II.5 Summary

III Conclusions

I. Horizontal CNT growth approach

I.1 Introduction

The superior properties of carbon nanotubes (CNTs) make them good alternatives to Cu for future interconnects. However, their adoption is limited by process integration and low CNT area densities. Integration schemes were developed for vertical interconnects (vias), with CNT densities approaching the required value of $3 \cdot 10^{13} \text{ cm}^{-2}$. However a resistance vs. length plot (Fig 1) shows a much larger advantage over Cu for CNT lengths over 1 micron, relevant for horizontal interconnects. Despite this potential, integration schemes for CNTs for horizontal interconnects are much less advanced than those for vertical interconnects with CNTs or graphene [1, 2]. Here, we show how to integrate CNTs as horizontal lines on 200 mm wafers, using vias filled with either metal or CNTs.



I.2 Technology developments

The initial idea of the project was based on the bridging of trenches with SWCNTs. Trenches are made in doped polysilicon with various geometries (see I.2.2). The objective was thus to bridge the two sides of the trench with high density CNT bundles.

The points to develop in order to be able to do that are:

- _Catalyst localisation on particular vertical structures
- _Growth of CNTs on these surfaces
- _Self connection of the tubes during growth

I 2.1 Growth Test structures

The horizontal test structures made by Intel have been described in Deliverable 3.3; the information on this structure is included here simply to aid the understanding of D3.5.

In each cavity of the chip there are different test units with various electrode patterns as presented figure 3. The gap between the electrodes varies between 300 to 5000nm.

Different electrode to insulating material geometries have been tested (Fig 4).

The structure called non undercut (NU) is composed of electrodes which sit perpendicular to the substrate.

The undercut structure (U) has an over etching of the insulating material previously done to avoid short-circuits of the structure if catalyst removal on the insulator is not complete.

The deep undercut (DU) was designed to have suspended CNTs and to have a different interaction between growing tubes and the substrate.

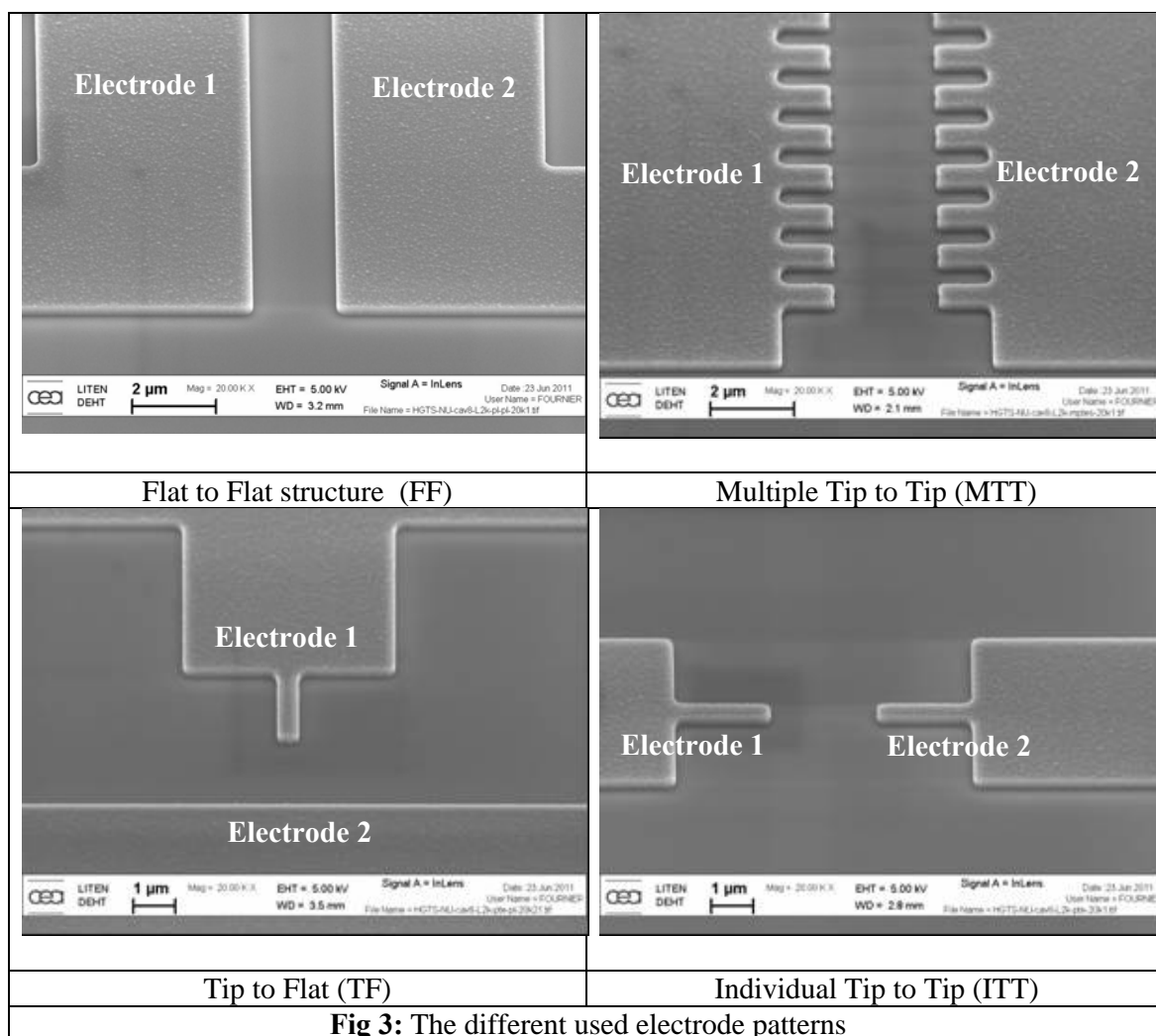


Fig 3: The different used electrode patterns

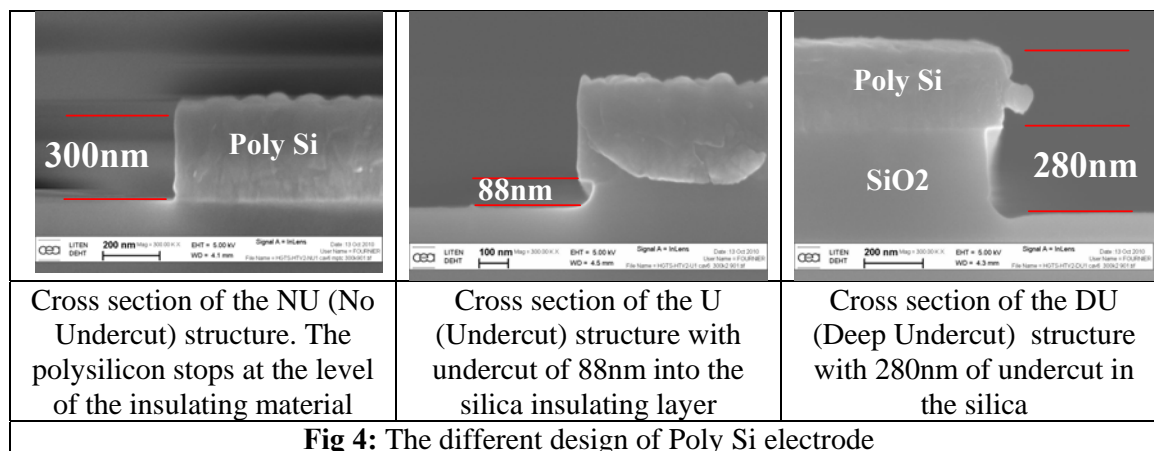
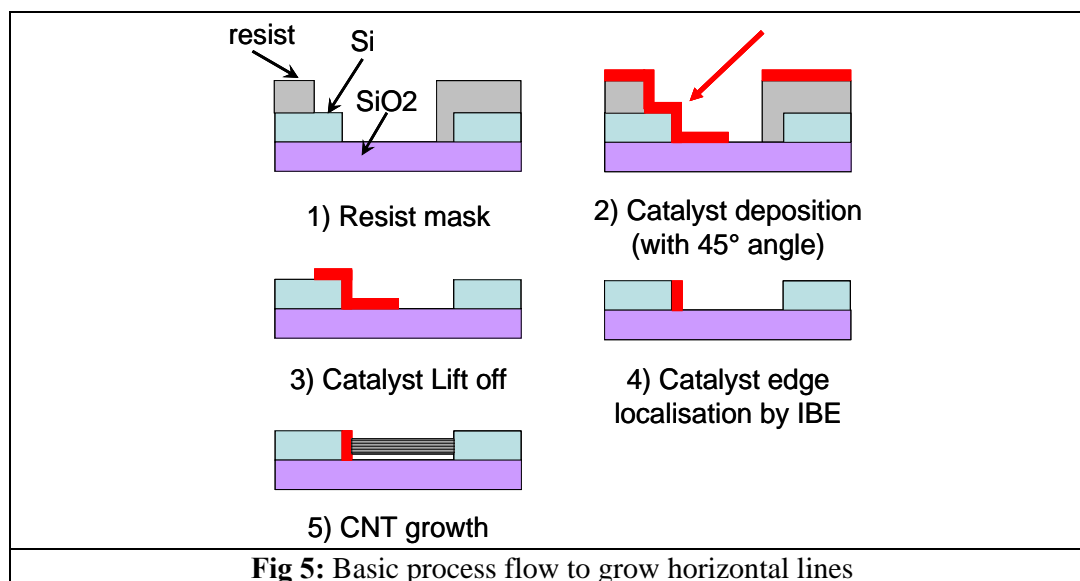


Fig 4: The different design of Poly Si electrode

I.2.2 Process flow

The catalyst localisation on the vertical edge of a trench is difficult. With the available catalyst deposition technology by PVD the flux of material is directional. Attempts of deposition with catalyst flux perpendicular to the structure gives very high catalyst thickness on the flat surface and lift off problems. Thus catalyst is deposited at 45° from normal incidence which allows for a more conformal catalyst deposition. The basic process flow is described in figure 5.



Most of the sample is covered by a resist mask which allows exposure of the edges where catalyst has to be deposited. Some catalyst is nevertheless deposited on unwanted horizontal surfaces [Fig 5 (2)]. After catalyst deposition the resist is lifted off [Fig 5 (3)] and the remaining catalyst is etched by ion beam etching [Fig 5 (4)]. The tubes are grown and self contact the opposite edge of the trench.

I.2.3 Catalyst integration

The μm thick photo resists deposited on the polysilicon structure (Fig 6) induces shadowing when the catalyst is deposited at 45° incidence; thus the units with gap electrodes smaller than $1\mu\text{m}$ have not been used because the catalyst is not nominal.

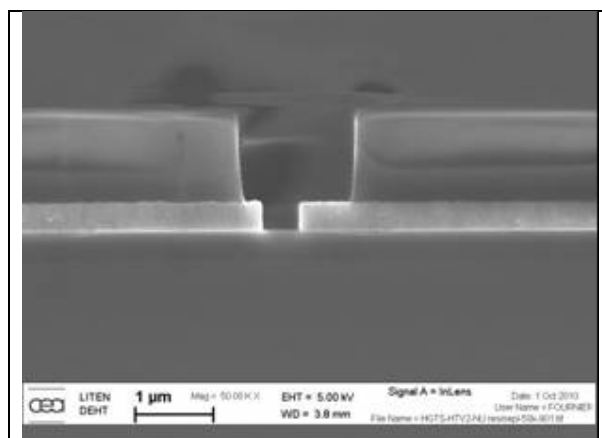


Fig 6: Resist layer deposited on the structure

The lift off of the resist occurs without problem except when the catalyst layer is too thick which prevents the action of the remover. The thickness limit is around 10 to 15nm.

The development of the IBE step has been tricky due to the difficulty in characterising the thickness deposited on the edge. The only practical way to do this was to control the efficiency of the etching by checking the results by CNT growth.

Thick catalyst layer has been used to start the development (Figs 8, 9) but the ultimate optimisation was achieved using CNT growth result.

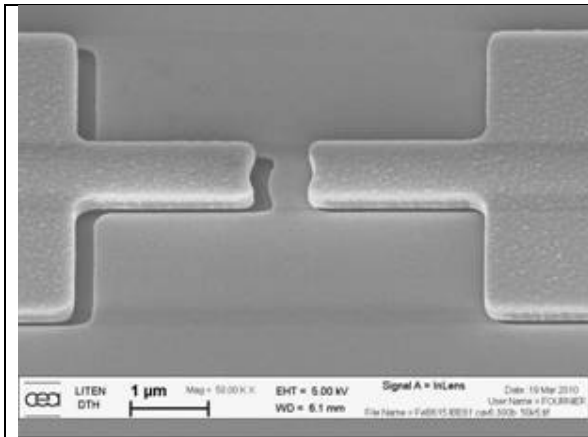


Fig 7: thick catalyst layer deposited at 45° which shows the catalyst shadowing by the electrodes

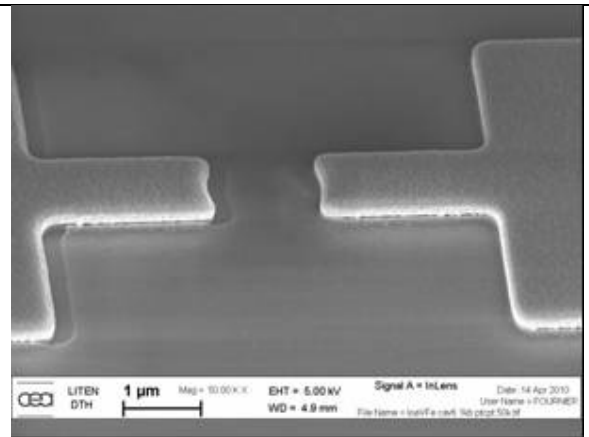


Fig 8: The structure of figure 7 after catalyst etching by IBE

The following features have been observed during the process development:

_Too long IBE is detrimental to growth while the growth anisotropy normally insures a wide process window. In fact this phenomenon is related to deposition of the etched material which may contaminate the catalyst. Particularly etching of the bottom insulating material may induce a capping of the catalyst detrimental for the growth.

_A stable IBE process needs a minimum etching time; thus a simple time ratio using etchings of thick layer is not applicable to thin layers of catalyst.

_When using a two layer system of catalyst composed of aluminium iron the complete stack must be etched, otherwise parasitic growth is always observed. We think part of the iron is implanted in the aluminium layer and is still active for growth when all the aluminium is not etched.

Finally an optimum IBE process has been determined for the used two layers catalyst (Fig 9). The etching time of 150s is just sufficient to etch the catalyst deposited on the bottom surface of the device; the remaining layer (less than 2nm) is without influence on growth and doesn't induce short circuits. The thickness of the catalyst layers before and after IBE is almost the same, no important deposit on the catalyst is observed which is confirmed by the CNT growth obtained.

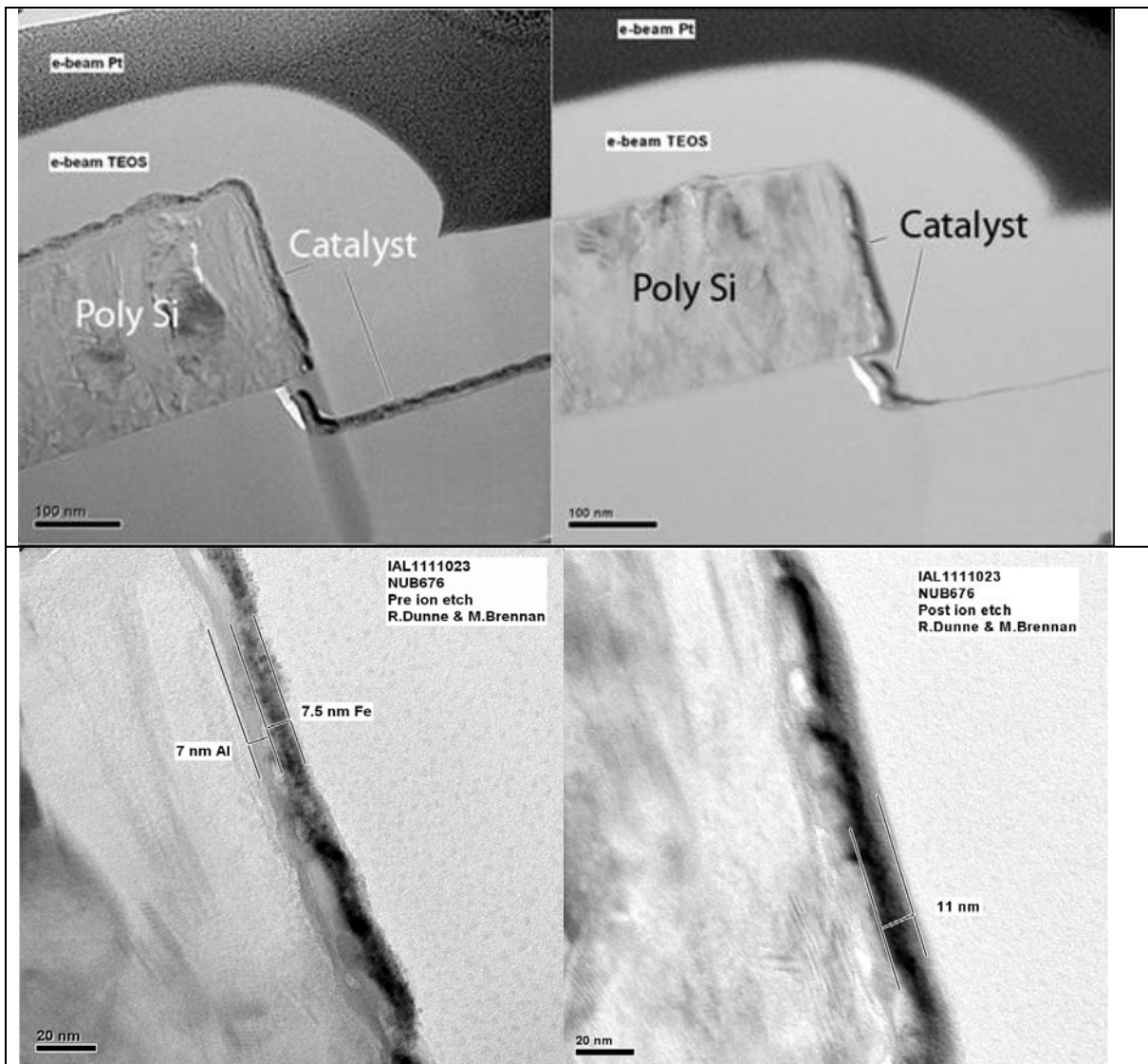
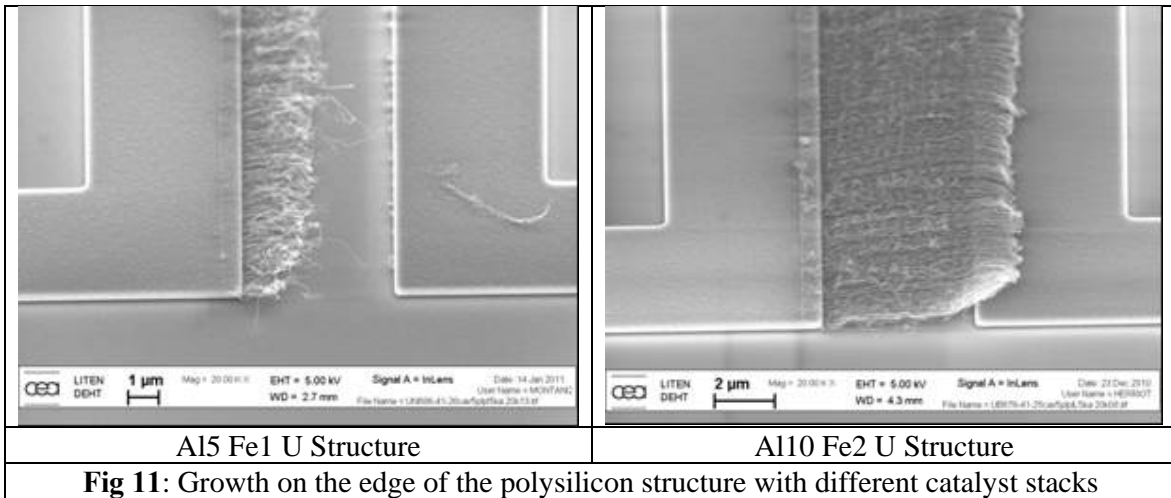
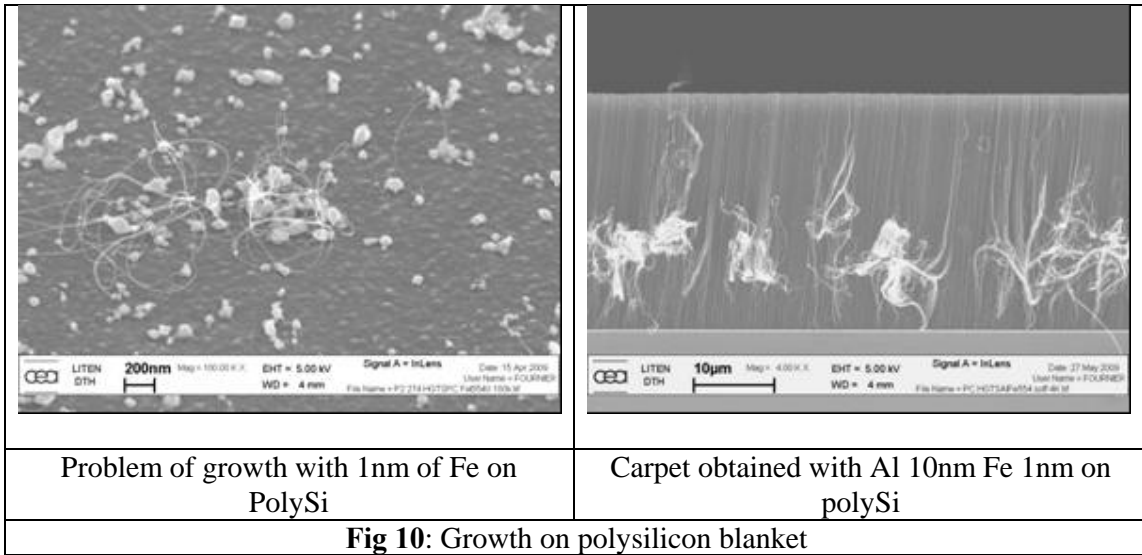


Fig 9: TEM Cross sections made by Intel which show the catalyst on U structure before IBE (on the top left) and after IBE (on the top right). The localisation on the vertical edge is obtained. The bottom images show the two layer catalyst before and after IBE

1.2.4 CNT Growth

Growth on poly silicon is much more difficult than growth on crystalline silicon and growth on the etched vertical wall is also different from the growth on the top surface of polysilicon. These differences come from the lower efficiency of the catalyst on polysilicon due to some diffusion of the catalyst on the grain boundary of the material. As a result, the growth can be sparse and the de-wetting of the catalyst differs from amorphous or crystalline materials. On the edge the difficulty is increased also by the complex shape of the structure and the difficulty in knowing the exact catalyst thickness due to planetary motion and shadowing. Very thin layers of iron can be rather inefficient (Fig 10); thus to increase the growth quality and the electrical contact we have developed a stack composed of aluminium and iron. Dense carpets on polysilicon are obtained with this catalyst (Fig 10). The transfer of this stack on the edge was constrained by the lift off problems. Normally at 45° incidence 15nm Al and 1.5nm of iron have to be deposited but this was too thick; thus our nominal thickness is 10nm Al 2nm iron. Thinner catalyst is less efficient (Fig 11).



The optimised recipe (standard process) used is as follow:

- _Al 10nm Iron2nm deposited at 45°
- _150s of IBE at 180W
- _Growth at 600°C

1.2.5 Results on the different electrode structures and density

Figure 12 presents the growth obtained for the different electrodes structures NU, U, DU with standard processes and for different gap widths. With NU and U good growth is obtained while for DU this is not the case. With this last structure the catalyst, also deposited on the silica below the polysilicon and two membranes, is growing which interacts unfavourably. In terms of density and CNT quality, the best results are obtained with NU structures. The achieved density determined by counting is close to 10^{11}cm^{-2} .

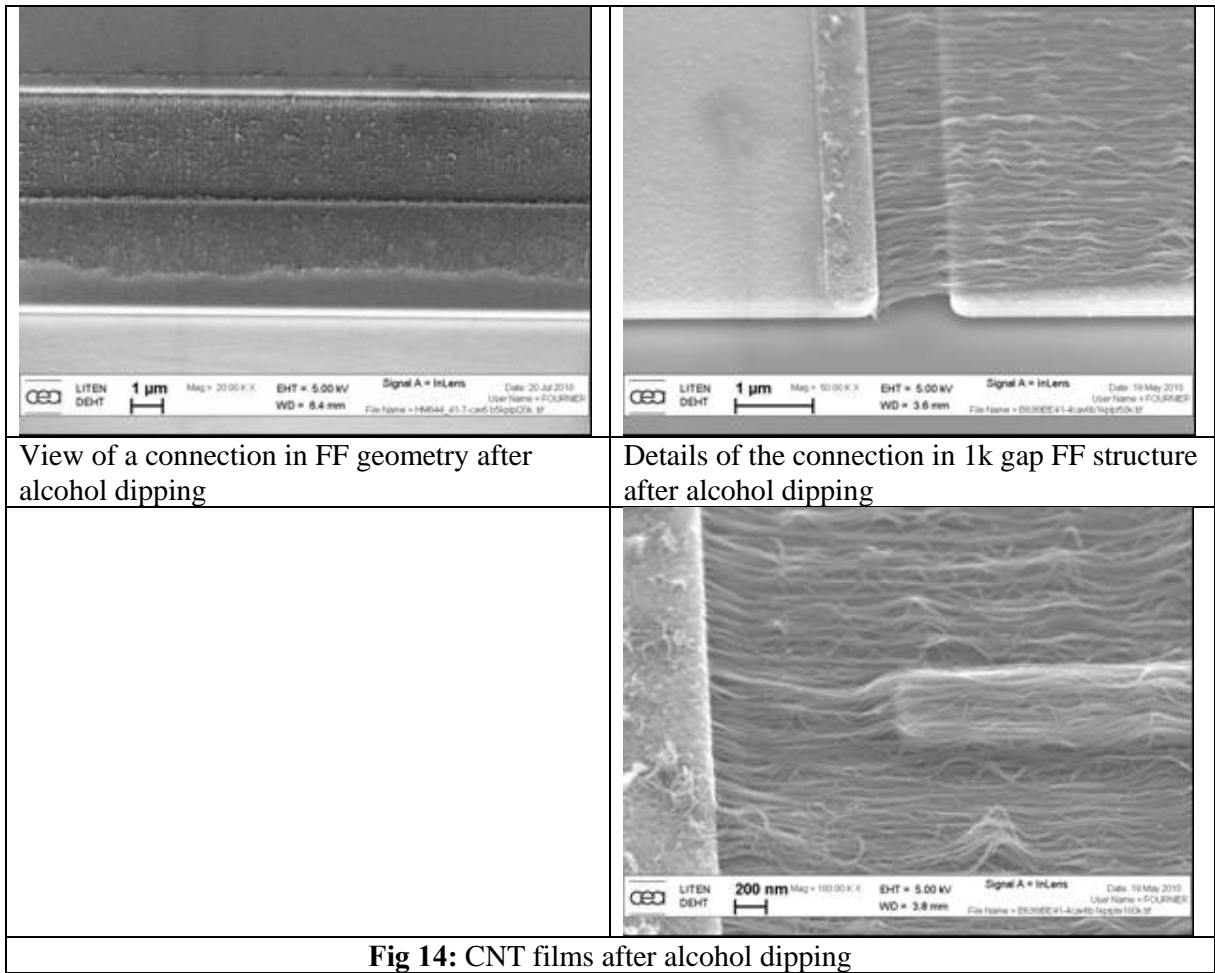
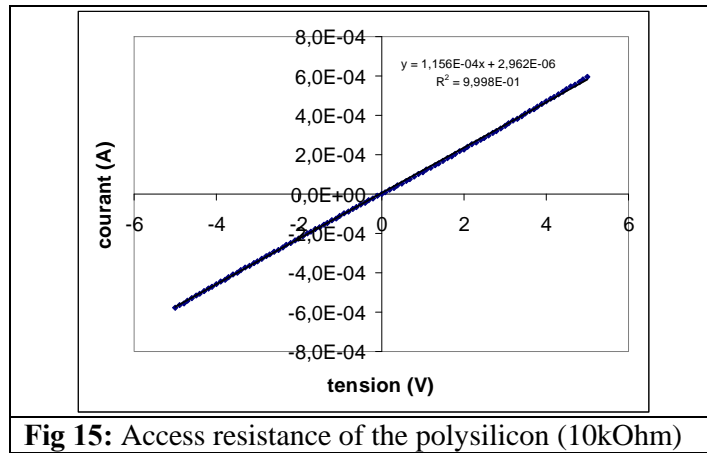


Fig 14: CNT films after alcohol dipping

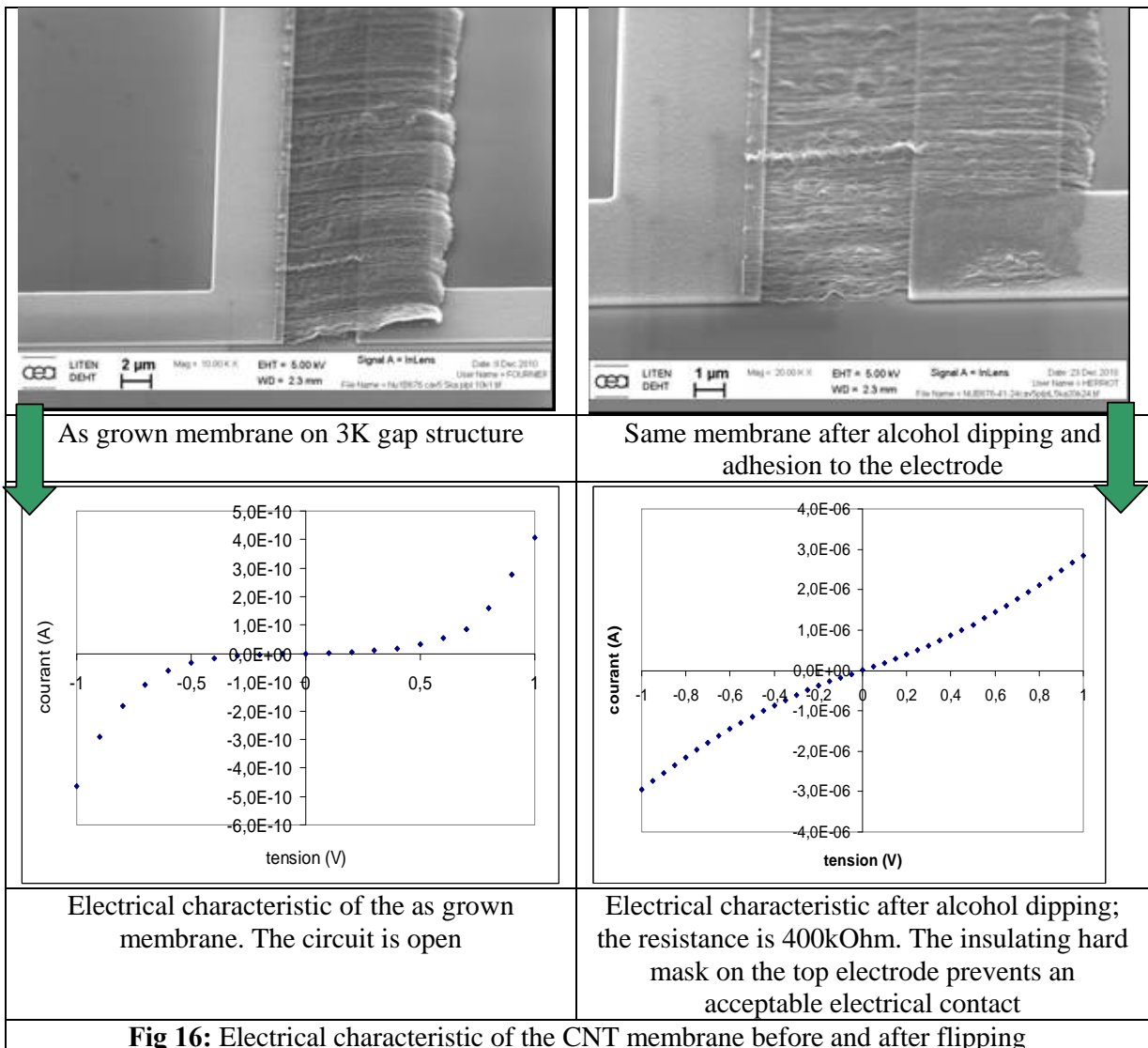
I.3 Electrical results

I.3.1 CNT growing from one edge

Each electrode pattern is connected to four pads allowing 2 point or 4 point probe measurements. The contribution of the electrodes resistance with two point probes measurements has been determined experimentally to be around 10kOhm (Fig 15). Thus this value has to be subtracted from the rough resistance obtained with 2 point probe characteristics. Two point probe resistance measurements have been done on FF structures just after growth and after alcohol dipping which flattens and adhere the tubes on the landing electrodes (Fig 16). As expected, without dipping the tubes are above the electrodes and an open circuit is measured. After dipping, the measured resistance decreases down to mega ohms with a best value of 0.4 MOhm.



The bad resistance is due to the insulating nature of the top electrode. Indeed the hard mask used to etch the trench in the polysilicon is still remaining. The hard mask was kept intentionally to insure a high quality vertical edge.



To confirm this point and try to measure the contact resistance trials have been done to pass through the hard mask by FIB. After making the trench, a Pt electrode is deposited by FIB. The process and example of samples made are presented (Fig 17).

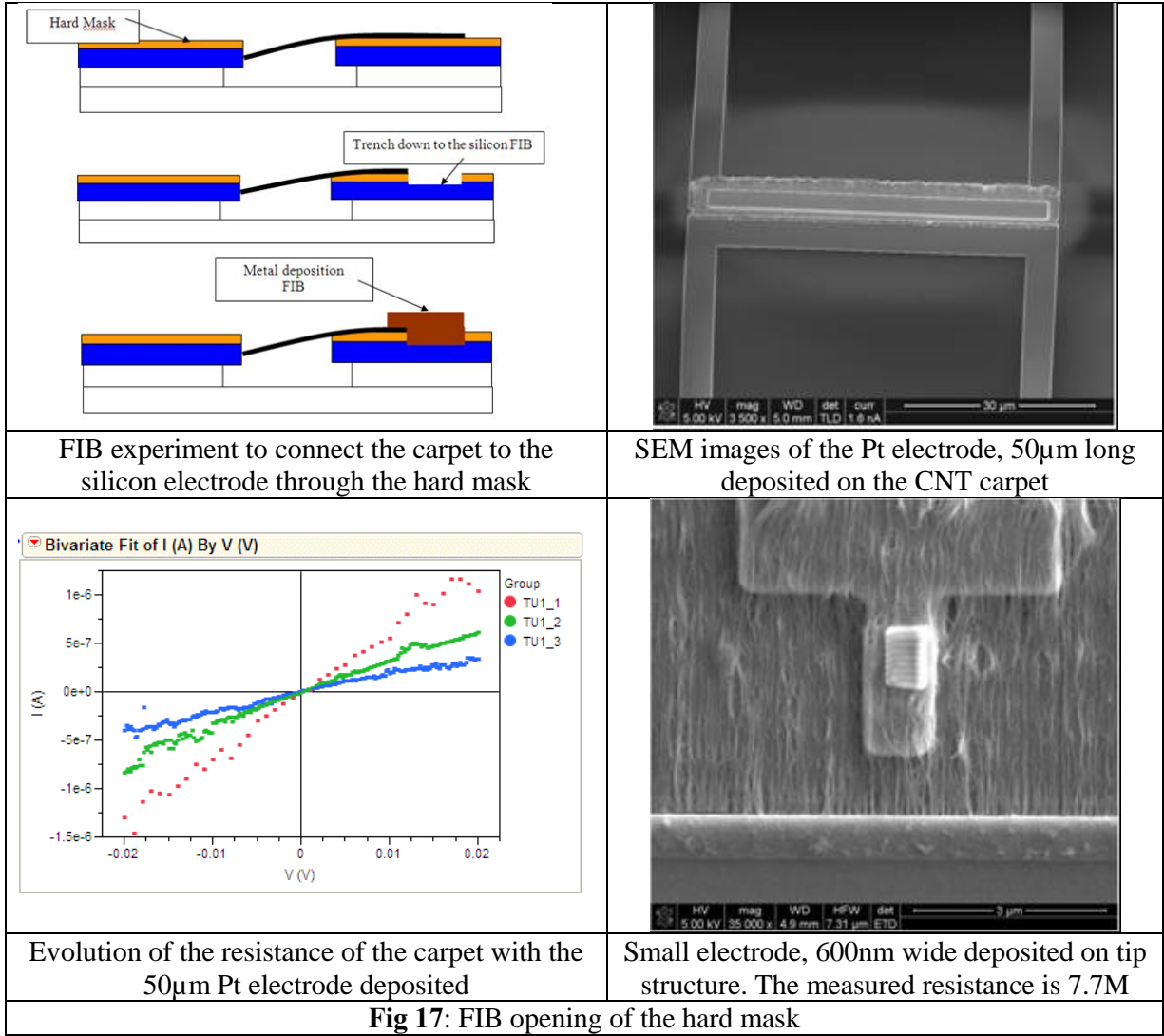


Fig 17: FIB opening of the hard mask

After FIB and Pt contact deposition the measured resistance was 15.2kohm for 50µm wide electrode and was degrading to 50kohm after several measurements. This evolution is not understood. With these values CNT contact resistance from one tube may be extracted.

The surface of the edge in contact with the electrode on the device is $50 \times 0.15 = 7.5 \mu\text{m}^2$. Assuming a CNT density around 10^{11} cm^{-2} it gives:

$$7.510^{-8} \times 10^{11} = 7.5 \cdot 10^3 \text{ tubes in contact with the platinum electrode}$$

Thus the contact resistance per tube assuming that the measured resistance is just due to the contact is

$$\text{Rc-line} = 1.5 \cdot 10^4 \times 7.510^3 = 1.12 \cdot 10^8 \text{ ohm/CNT}$$

The second experiment on tip (Fig 17) gives a resistance of 7.7Mohm for a much smaller electrode of 600nm.

In that case the contact resistance per tube is

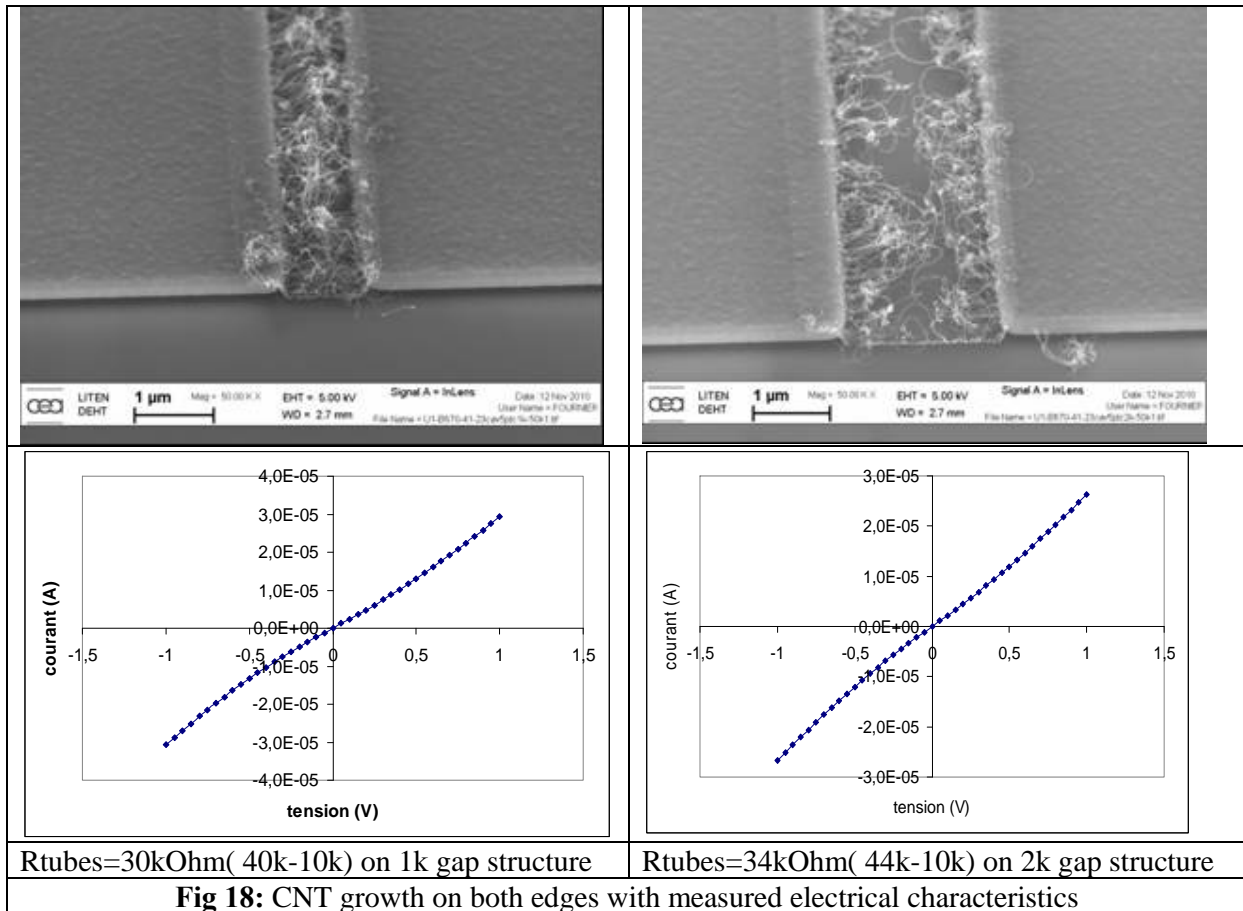
$$\text{Rc-line} = 90 \times 7.710^6 = 6.9 \cdot 10^8 \text{ ohm/CNT}$$

This resistance is higher by a factor six and that may partly due to the contact resistance between Pt and silicon which has less chance to be good due to the small contact area and possible oxide remaining on the Si. The order of magnitude is nevertheless similar.

I.3.2 CNT growing from two edges

Due to the difficulty in making a good electrical contact on the landing electrode because of the presence of the hard mask we have grown CNTs from both sides of the trench, in the hope that the connection between the tubes coming from both sides will be more acceptable than the connection through the hard mask.

So two successive catalyst depositions have been done (one to cover each edge), then the catalyst was lifted off and a longer IBE (360s) has been applied because the two layers of catalyst overlap on the bottom part of the device. The growth is rather sparse as seen in figure 18.



For 1μm and 2μm gaps the resistance is almost equivalent while it becomes 1.4 Mohms for 5μm gap where the tubes are not connected. Thus, the 30Kohm resistance is attributed to the contacts on both sides of the trench.

The surface of the edge exposed to catalyst on FF structure is $60 \times 0.15 = 9 \mu\text{m}^2$, assuming a CNT density around $5 \times 10^{10} \text{ cm}^{-2}$ to be conservative with two edges growth as compared with better single edge it gives

$$9 \times 10^{-8} \times 5 \times 10^{10} = 9 \times 10^3 \text{ tubes grown on each side of the trench}$$

Thus the resistance per tube bridging the electrodes with the 30kOhm connection measured is

$$R_t = 3 \times 10^4 \times 9 \times 10^3 = 2.7 \times 10^8 \text{ ohm}$$

Assuming that the contact resistance between tubes is identical or negligible as compared with the contact resistances between CNT and silicon we estimate the contact resistance between CNT and Si on the line structure to be:

$$0.9 \cdot 10^8 \text{ ohm} < R_{c\text{-line}} < 1.35 \cdot 10^8 \text{ ohm}$$

This value is pretty close to the estimated value coming from the FIB experiment.

This contact resistance value can be compared with our results in vias.

The best measured via resistance on Al is about 600ohm per μm^2 .

In that case the CNT density is 10^{12} cm^{-2} ; thus 10^4 CNTs are paralleled in the vias leading to a contact resistance between CNT and aluminium to be in between

$$3 \cdot 10^6 \text{ ohm} < R_{c\text{Via}} < 6 \cdot 10^6 \text{ ohm}$$

Depending on the weight attributed to the top contact.

Roughly speaking the contact resistance is between one and two orders of magnitude higher on the lines than on the integrated vias. This difference is attributed to the contact with silicon which adds extra insulating material (SiO_2) and contributes to the barrier.

I.4 Summary

A wafer level compatible technology has been developed to localise the catalyst on the vertical edge of the structure in order to make horizontal connections.

The best catalyst stack to grow CNTs horizontally is a two layer system composed of 10nm aluminium and 2 nm iron deposited at 45° from the sample normal. This stack allows CNT growth with a density around 10^{11} cm^{-2} at 600°C .

The localisation of the catalyst has been done by a combination of resist lift off and ion beam etching. The best parameters for Etching are 150s at 180W for an incidence of 90° .

The etching time must be sufficient to etch both iron and aluminium otherwise residual growth on unwanted surfaces is observed.

The best structures among those developed are the structure without undercut in the silica.

With this technology, self contacting of the growing tubes has never been achieved on the facing electrodes while beautiful membranes have been grown almost horizontally.

After growth, alcohol dipping allows adhesion of the membrane on the device surfaces and increases the density without large deformations.

Contact resistance per tubes has been measured with different configurations and converges consistently towards a resistance around 10^8 ohms per CNT which is at least two orders of magnitudes higher than the project results on vias. This difference is attributed to silicon oxide remaining on the polysilicon surface. A more complex contacting area with silicide is probably needed to lower the contact resistance. The developed technology will be compatible with such a device.

The process flow of figure 5 is not complete because unfortunately contact deposition has to be made after CNT growth.

A much better catalyst deposition technique for this kind of structure is certainly ALD deposition of iron oxide which is conformal and will largely simplify the technology. Metal electrodes instead of silicon ones have to be made to improve the results.

Improvements are possible but considering the achieved density and contact resistance another option to make horizontal lines described below has been studied.

II Vertical growth with flipping approach

II.1 concept

The density of horizontally grown CNTs is less than the density achieved by using vertical growth so by using redirection of the CNTs by alcohol dipping it is possible to use the high density achieved in vias to make connections.

With our process, very dense (around 10^{13} cm^{-2}) and long bundles (20 μm) are grown from vias (Fig 19). In this example the density on the vias (reported to the via area) is $3 \cdot 10^{12} \text{ cm}^{-2}$ while in the bundle after tube focusing and densification the density is $9 \cdot 10^{12} \text{ cm}^{-2}$.

Thus connections with the requested CNT density and diameter around 100 or 200nm are possible. One main advantage by flipping starting from vias is the possibility to make a via to line connection without interface and thus it minimizes the weight of the contact resistance.

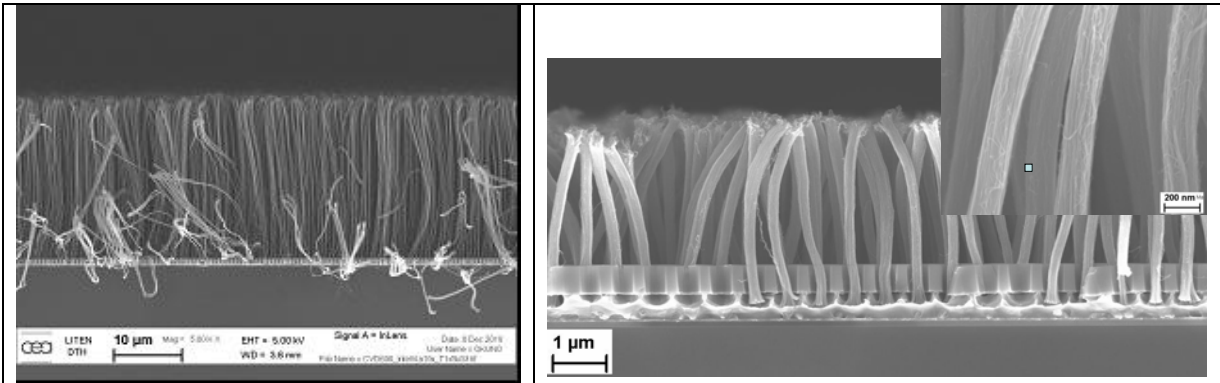


Fig 19: On the left long bundles (20 μm) emerging from vias. On the right 200nm diameter bundle with a density of $9 \cdot 10^{12} \text{ cm}^{-2}$ after densification

II.2 Process flow

The used samples are modified HTV structures with a resist mask which allow deposition of the catalyst on one electrode. The process flow is given (Fig 20).

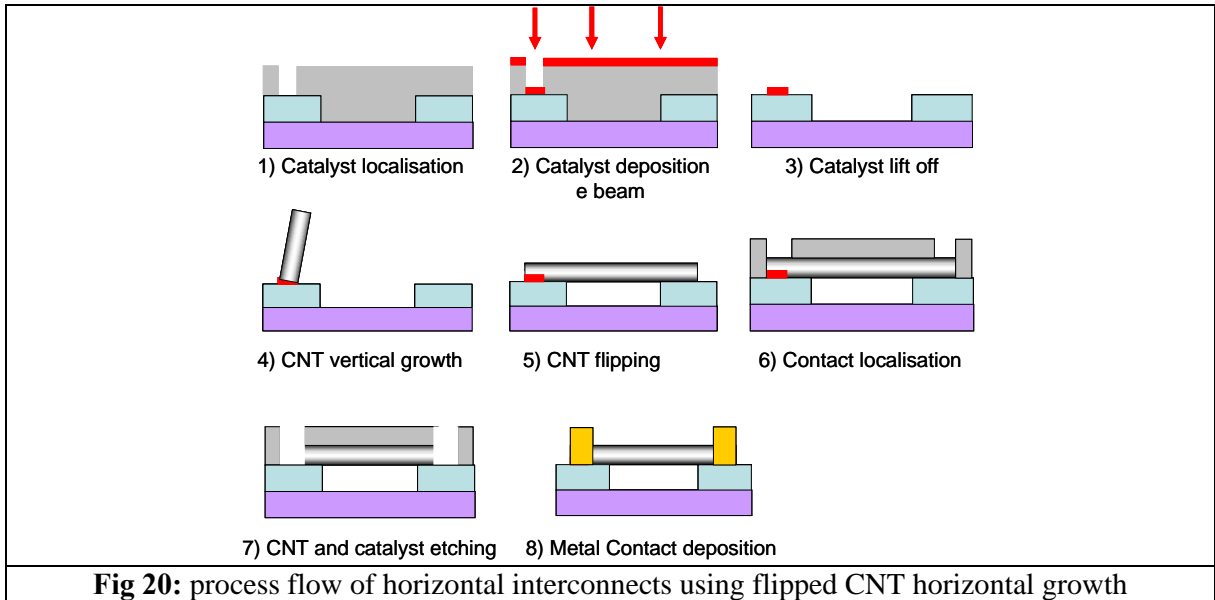


Fig 20: process flow of horizontal interconnects using flipped CNT horizontal growth

A resist mask is used to localize the catalyst on one electrode, then the catalyst is deposited (2) and the resist is lifted off (3). The CNTs are grown with a pre-inclined direction (4) with respect to the normal in order to flip them in the right direction on the electrodes (5). A resist mask is deposited (6) to define the contact area on the CNTs. The initial growth area can be etched (7) which allows the full decoupling of the growth materials to the contacting ones.

II.3 Devices

A new resist mask has been made in order to define resist box on the electrodes. The width of this boxes are 0.5, 0.75, 1, 1.5 μm (Fig 21). It has been deposited on FF, TF and MTT structures.

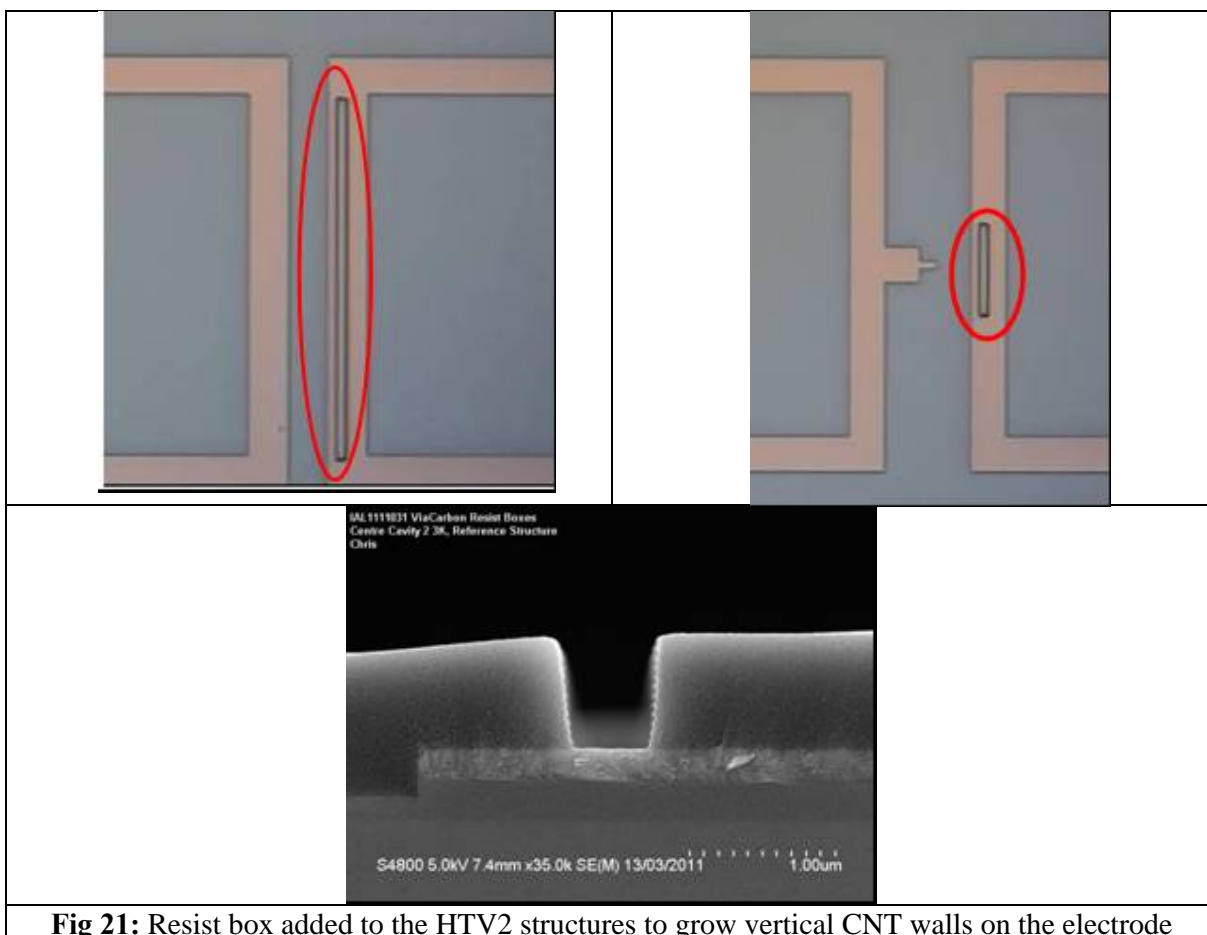
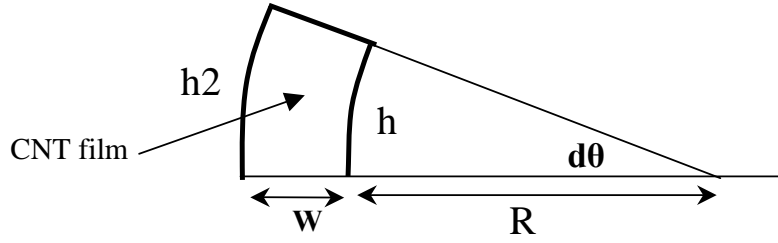


Fig 21: Resist box added to the HTV2 structures to grow vertical CNT walls on the electrode

II.4 Flipping technology

II.4.1 Control of the flipping direction

Vertical CNT walls have a tendency to bend naturally and this bending direction must be controlled in order to predetermine the direction of flipping of the wall when the dipping will be done. This bending is determinist; thus it means that on a chip all the walls will bend more or less in the same direction. This bending depends on the width of the wall and ultimately on the aspect ratio between width and height. The bending is induced by different growth rates between the tubes growing in the wall; thus by different tube lengths. As the tubes interact, the equilibrium of the wall is no more a flat and vertical shape. To control the bending we have to control the location of the fast growing tubes. The growth rate is inversely proportional to the catalyst thickness because the carbon flux is dependant on the gradient of the carbon in the catalyst

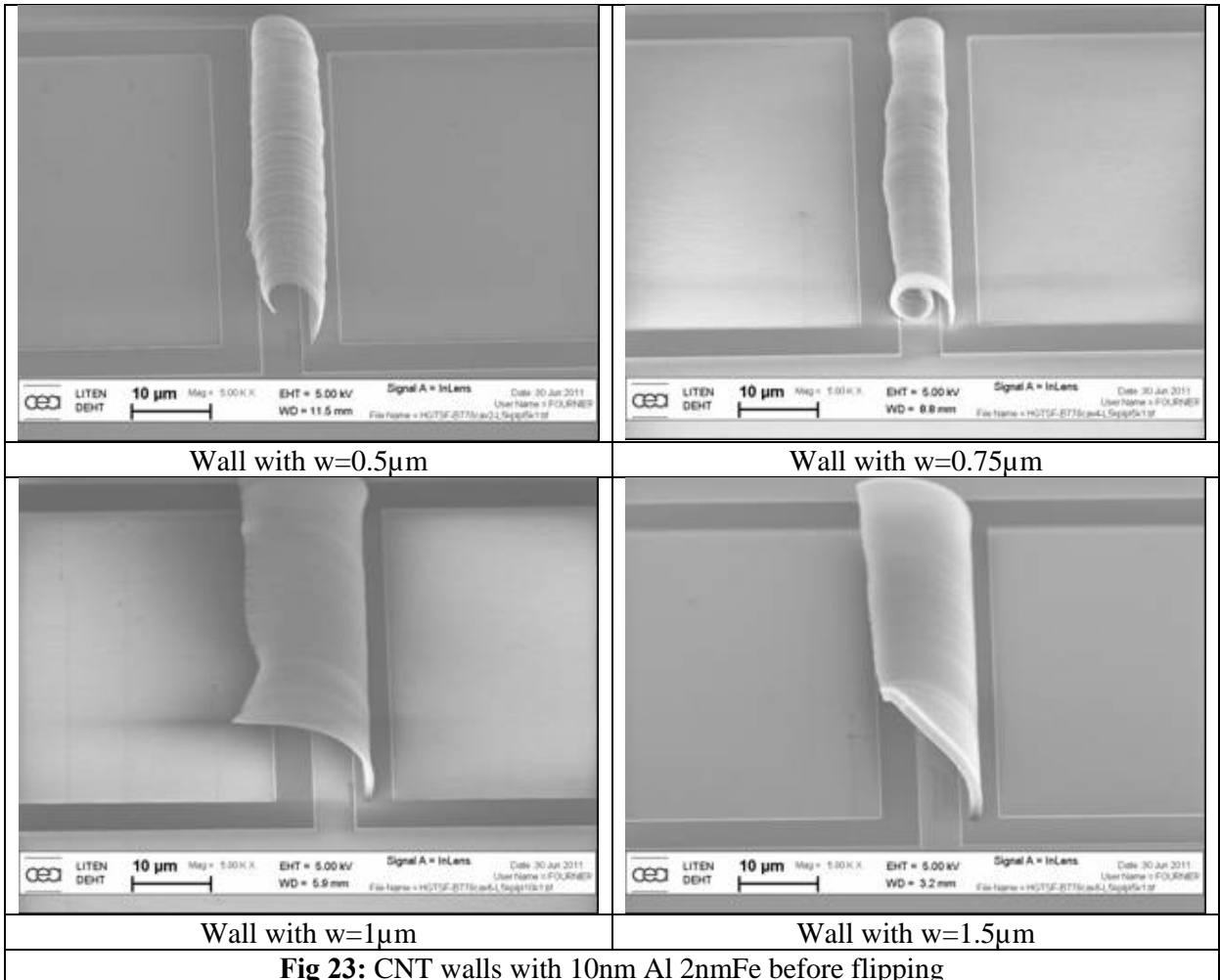


$$R d\theta = h \quad d\theta = \frac{h2 - h}{w}$$

$$\text{Thus } R = \frac{gw}{dg} \text{ with } h = gt$$

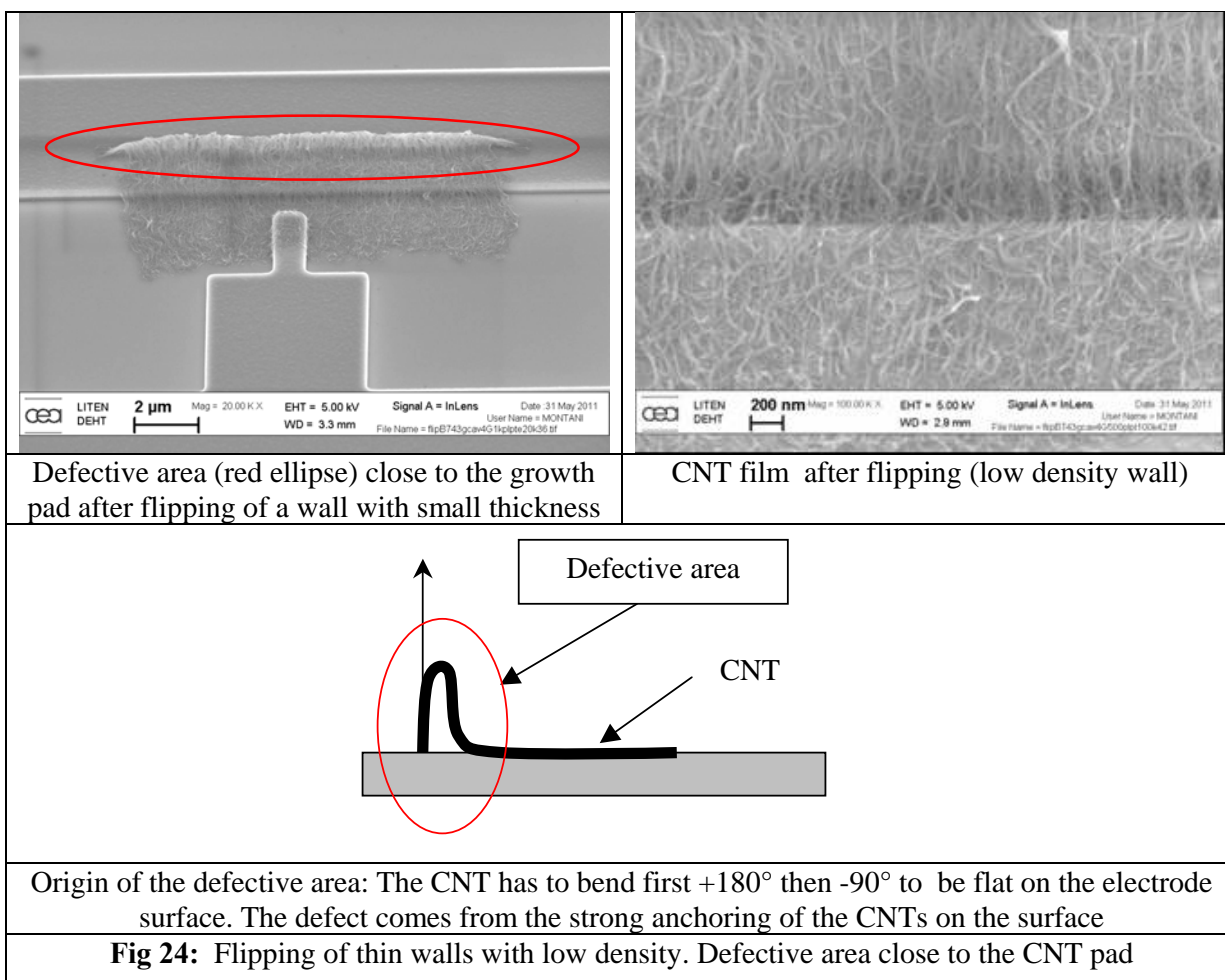
g is the growth rate and dg is the growth rate variation induced by the catalyst thickness variation de . So the curvature radius of the film is $R = -\frac{ew}{de}$ and this curvature is proportional to the wall thickness which is qualitatively observed in figure 23.

In our experiments, the curvature radius of the thin CNT wall must be increased so it means that the catalyst gradient is too important. In some cases a roll is formed and good flipping is no longer possible.

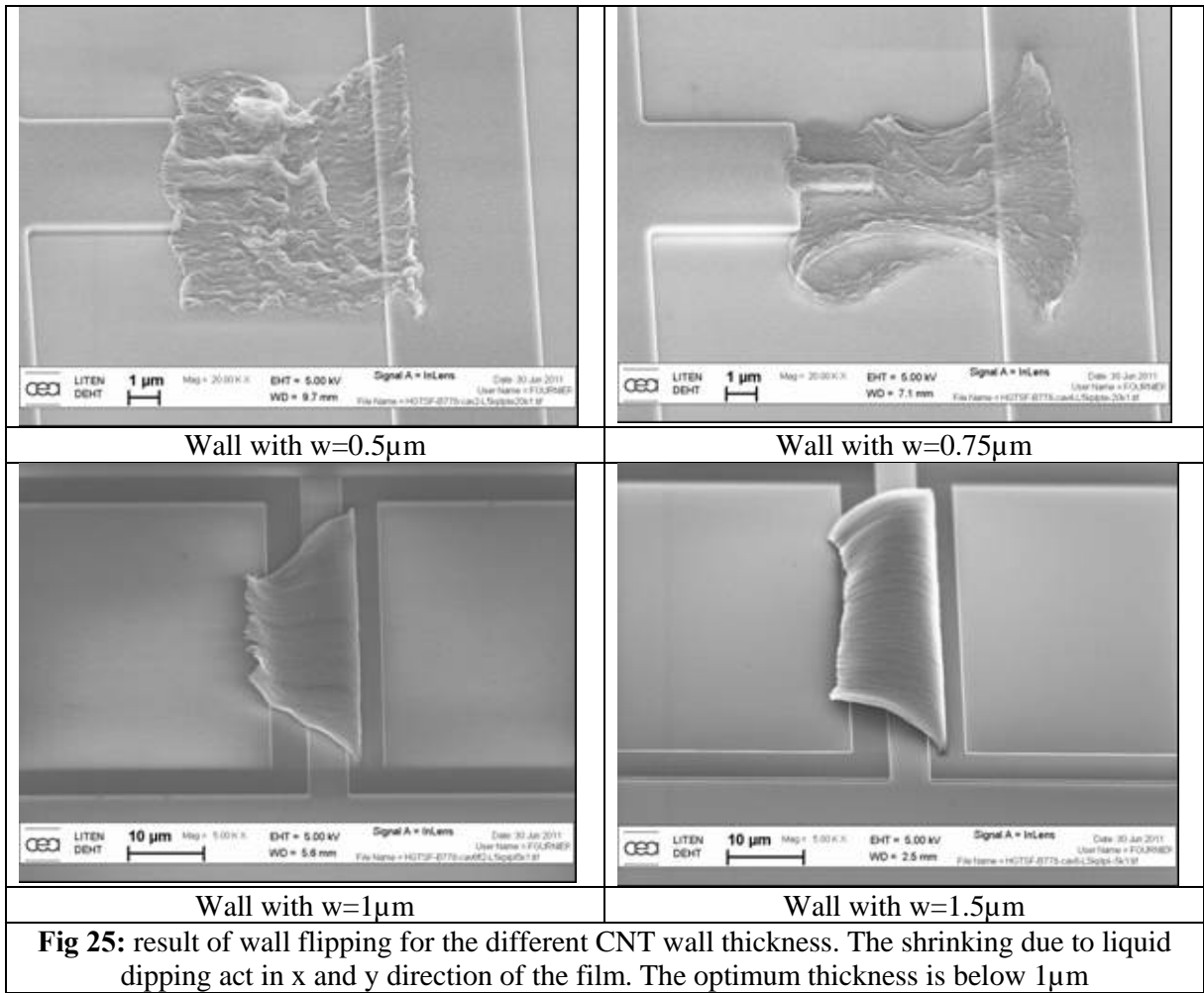


So we have to decrease the deposition angle of the catalyst to correct the observed problem.

After dipping when the wall is thin a defect is observed at the level of the catalyst pad (Fig 24). This defect comes from the vertical direction of growth and the CNT strength. Due to the location of the electrode the wall has to reverse its direction first with an angle of $+180^\circ$ then to bend with an angle of -90° . For a thick wall such direction change is not easily possible and the wall doesn't always adhere to the surface (Fig 25).



The optimum wall thickness with this geometry and dense walls is below $1\mu\text{m}$. Due to the curvature of the CNTs on the sample we have prepared the flipped thin walls are not yet perfect. The density of the walls estimated by densification is around 0.8 to $1 \cdot 10^{12} \text{ cm}^{-2}$. The growth has not yet been optimized to increase the density but it is perfectly possible to achieve equivalent density to that in vias.



II.4.3 Flipping of CNTs from via and trenches

One of the identified problems is the need to have a very strong curvature to adhere the walls on the surface. This curvature produces a defective area close to the catalyst pad when the film is small and contributes to the misalignment of the film during flipping. For thick walls, the flipping is difficult due to the high stiffness of the wall. This curvature requirement is due to the geometry of the electrode, much better results would be obtained if the growth catalyst pad was below the electrode. In that case, the requested bending is just 90° and much more tractable by the CNT film. Trials have been made in these directions and the results are given in figure 26. Trenches of 250nm existing in VTV have been used to test the idea. As can be seen (Fig 26) the flipping results are much better and well aligned films with a thickness of 70nm have been obtained. The films are longer than $20\mu\text{m}$ and the alignment of the tubes on the surface while not yet perfect is far better. Films growing in the perpendicular directions have been successfully flipped.

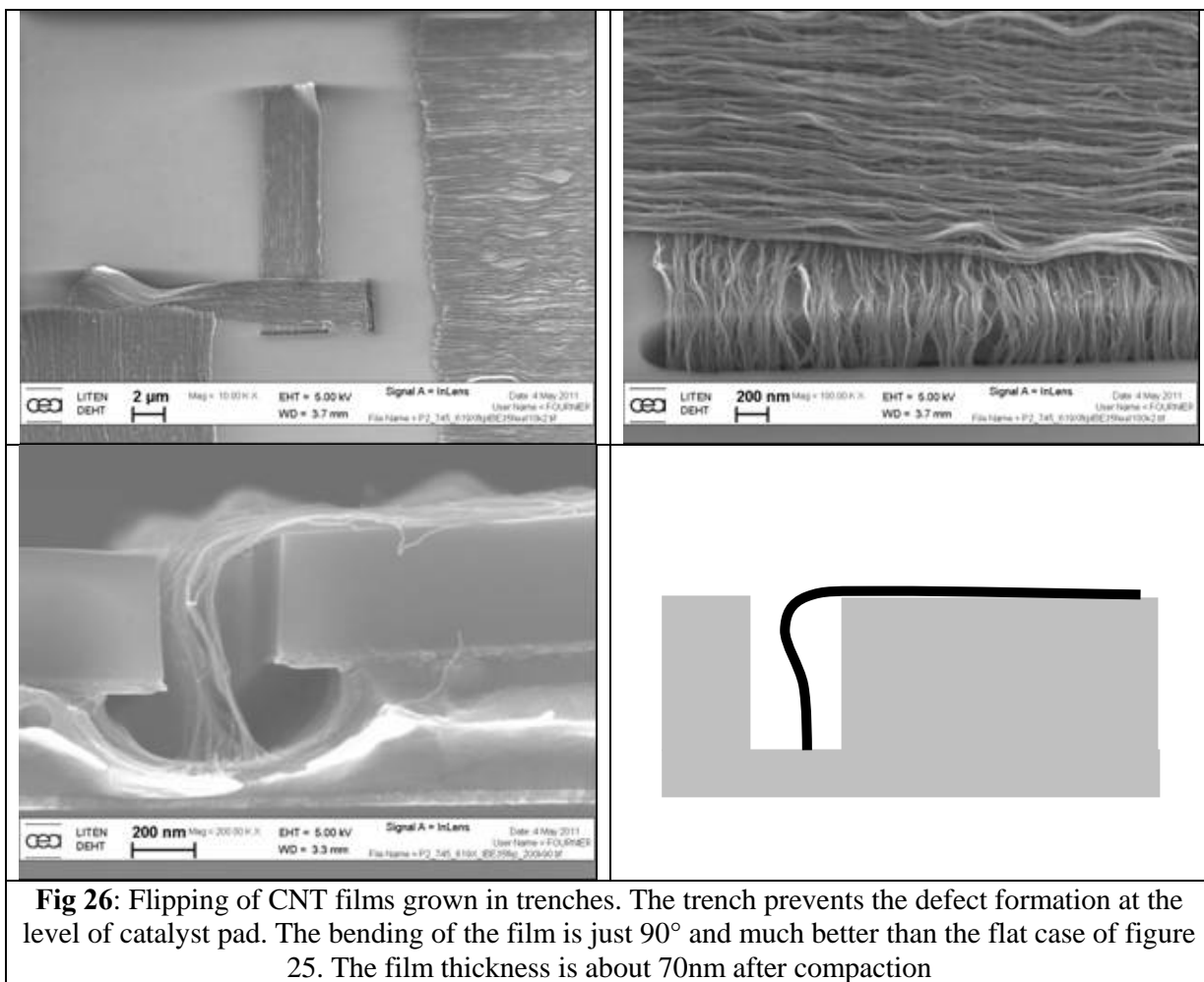


Fig 26: Flipping of CNT films grown in trenches. The trench prevents the defect formation at the level of catalyst pad. The bending of the film is just 90° and much better than the flat case of figure 25. The film thickness is about 70nm after compaction

II.5 Summary

Vertical CNT growth to make horizontal lines has been investigated. Walls with densities close to 10^{12} cm^{-2} and with thickness ranging between 0.5 and 1.5 μm have been grown. The wall bending has been controlled which allows flipping of the walls in the right direction to make devices. The bending and flipping direction is controlled by a small thickness gradient of catalyst. This gradient also induces the radius of curvature of the wall. This radius is proportional to the wall thickness; thus thin walls with too large gradients may form rolls.

The flipping of these walls has been performed. Due to the location of the catalyst pad on the electrode, the requested curvature of the wall to adhere on the surface is high and the defective area is created by the flipping process close to the roots of the CNTs. With thick walls, complete flipping can be difficult.

A much better geometry is to put the growth pad in trenches with the landing area for the wall above the catalyst pad. With such geometry dense films with length close to 20 μm and thickness of 70nm have been successfully grown and flipped on the surface. The CNT alignment after flipping is good.

III Conclusions

We have explored two different process flows to make long horizontal connections in CNTs. A new original process compatible with wafer integration has been developed which allows decoupling of the CNT growth area from the contacting area. In Table 1 a benchmarking of the processes is provided. We think the best solution for interconnects is that which involves the flipping from the trench or via of dense CNT bundles. The horizontal growth while difficult is now mastered and can be used to make membranes. It has the advantage to provide defect free well aligned CNT films on surfaces.




Technology	Horizontal growth	Flip from electrode	Flip from trench or via
			
Catalyst localisation	Hard --	Easy ++	Easy ++
CNT growth (density)	Low -	High +	Very high ++
Flipping	Very easy ++	Difficult -	Easy +
Alignment of the film after flipping	Very good ++	Medium - (may be improved)	Very good ++
Scaling toward lower dimension	Difficult TBD -	Difficult TBD -	Easier +
Electrical contact	Hard excepted when reported +	Hard excepted when reported +	Hard bottom contact excepted when reported +
Via to line connection	Need some metal pad -	Need some metal pad -	Dual damascene possible ++
Possible progress	Density contacts	contacts	contacts

Table 1: attempt to benchmark the different horizontal technologies investigated

References

- [1] M Nihei, et al, Jpn J App Phys 43 1856 (2004)
- [2] Y Awano, et al, IEDM (2009) p10.1