CARBON NANOTUBE USING ELECTRONICS

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ABSTRACT:

We evaluate the potential of carbon nanotubes (CNTs) as the basis for a new nano electronic technology. After briefly reviewing the electronic structure and transport properties of CNTs, we discuss the fabrication of CNT field-effect transistors (CNTFETs) formed from individual single-walled nano tubes (SWCNTs), SWCNT bundles, or multi walled(MW) CNTs. The performance characteristics of the CNTFETs are discussed and compared to those of corresponding silicon devices. We show that CNTFETs are very competitive with state-of-the-art conventional devices. We also discuss the switching mechanism of CNTFETs and show that it involves the modulation by the gate field of Schottky barriers at the metal-CNT junctions. This switching mechanism can account for the observed sub threshold and vertical scaling behavior of CNTFETs, as well as their sensitivity to atmospheric oxygen. The potential for integration of CNT devices is demonstrated by fabricating a logic gate along a single nano tube molecule. Finally, we discuss our efforts to grow CNTs locally and selectively, and a method is presented for growing oriented SWCNTs without the involvement of a metal catalyst.

Keywords—Carbon nanotubes (CNTs), field-effect transistors (FETs), molecular electronics, nanoelectronics.

I. INTRODUCTION

Carbonnanotubes (CNTs)are hollow cylinders composed of one or more concentric layers of carbon atoms in a honeycomb lattice arrangement. Multiwalled nanotubes (MWCNTs) were observed for the first time in transmission electron microscopy (TEM) studies by Iijima in 1991 [1], while single-walled nanotubes (SWCNTs) were produced independently by Iijima [2] and Bethune [3] in1993.

SWCNTstypicallyhaveadiameterof1–2nmand alength ofsever micro meters. The large aspectratio makes then an- otubes nearly ideal one-dimensional (1-D) objects, and as such the SWCNTs are expected to have all the unique properties predicted for these low-dimensional structures[4]–[7].In addition, as we discuss below, depending on the detailed arrangement of the carbon atoms the SWCNTs can be metallic or semiconducting [8], [9]. Furthermore, the C–C bonds in CNTs are very strong, resulting in an extremely high me- chanical stability (Young's modulus about ten times higher than that of steel) and chemical inertness. The strong, cova- lent bonding also leads to near perfect side-wall structures with very few defects.

CNTs are currently considered as promising building blocks of a future nanoelectronic technology. This is not simply due to their small size but rather to their overall properties. In fact, many of the problems that silicon tech- nology is or will be facing are not present in CNTs. Below we list some of these CNT properties and their implications for electronics.

1) Carrier transport is 1-D. This implies a reduced phase space for scattering of the carriers and opens up the possibility of ballistic transport. Correspondingly, power dissipation is low. Furthermore, as we discuss in Section II, their electrostatic behavior is different from that of silicon devices with implications on screening and electron/holetunneling.

2) All chemical bonds of the C atoms are satisfied and there is no need for chemical passivation of dangling bonds as in silicon. This implies that CNT electronics would not be bound to use SiO as an insulator. High dielectric

constant and crystalline insulators can be used, allowing, among other things, the fabrication of three-dimensional (3-D)structures.

3)

ThestrongcovalentbondinggivestheCNTshigh me- chanical and thermal stability and resistance to elec- tromigration. Current densities as high as 10 A/cm can be sustained[10].

4) Their key dimension, their diameter, is controlled by chemistry, not conventionalfabrication.

5) In principle, both active devices (transistors) and in- terconnects can be made out of semiconducting and metallic nanotubes,respectively.

We see that the properties of the SWCNTs are trulyremark- able. However, finding ways to effectively exploit these properties remains a challenge. In the rest of this paper
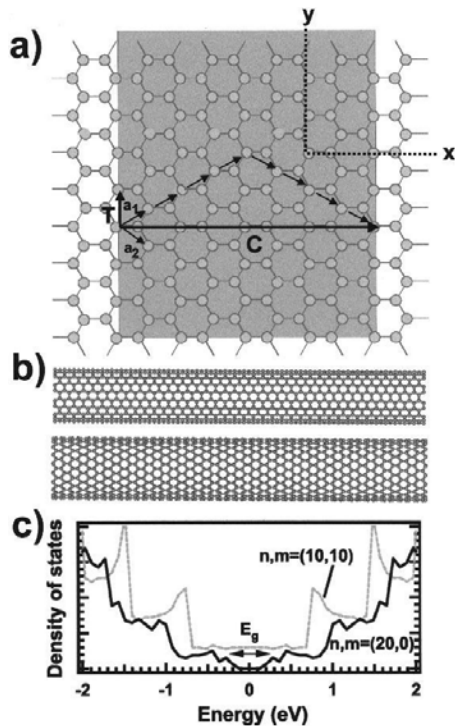

Fig. 1. (a) Description of the structure of CNTs in terms of the chirality vector C and the (n,m) indices. The example shown involves a (4,4) tube. (b) Atomic structure of a metallic (10,10) CNT (top) and a semiconducting (20,0) CNT (bottom), and (c) the corresponding density of states versus energy plots.

we will review the electronic structure of the CNTs and then present our efforts to fabricate nanotube transistorsand simple integrated circuits and understand the underlying de-

vicephysics.

II. ELECTRONIC STRUCTURE OF CARBON NANOTUBES

The electronic structure and electrical properties of SWCNTs are usually discussed in terms of the electronic structure of a graphene sheet (a layer of graphite) [4]–[9]. The SWCNT can be thought of as being formed by folding a piece of graphene to give a seamless cylinder. The cir- cumferenceof the nanotube is expressed by the so-called chirality vector, , connecting two crystallographically equivalent sites of the two-dimensional (2-D) graphene sheet (seeFig.1). ,where and are the unit vectors of the hexagonal honeycomb lattice, so that any nanotube can be described by a pair of integers (n,m) that define its chiral vector. For example, the chiral vector shown in Fig. 1(a) describes a (4,4) nanotube. The unitshell of the nanotube is defined as the rectangle formed by and the 1-D translationalvectoridentified in Fig. 1. Also shown are the atomic structures of a (10,10) and a (20,0) CNT [Fig. 1(b)] and their density of states [Fig.1(c)].

The interesting electrical properties of CNTs are due in a largeparttothepeculiarelectronicstructureofthegr aphene. Its band structure and its hexagonal first Brillouinzone
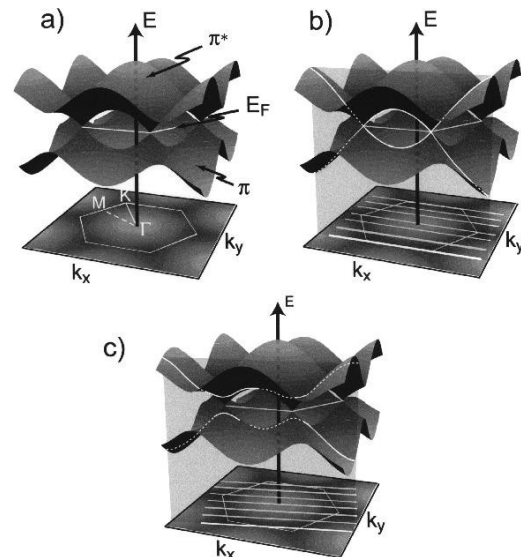

Fig. 2. (a). Band structure of a graphene sheet (top) and the first Brillouin zone (bottom). (b) Band structure of a metallic (3,3) CNT.
(c) Band structure of a (4,2) semiconducting CNT. The allowed states in the nanotubes are

cuts of the graphene bands indicated by the white lines. If the cut passes through a K point, the CNT is metallic; otherwise, the CNT issemiconducting. are shown in Fig. 2(a). The energy surfaces describing the valence and conduction states touch at six points (Fermi points) lying at the Fermi level. This unusual band structure has immediate consequences for the electronic properties of graphene. While allowed states exist at the Fermi level, the dimensionality of the system (2-D) results in a vanishing density of states when integrating over theFermisurface.Becauseofthisparticularsituation,graphene is a zero-gapsemiconductor.

Inthecaseofananotubethereisanadditionalquantization arising from the confinement of the electrons in the circum- ferential direction in the tube. This requires that the circum- ferential component of the wave vector can only take the valuesfulfillingthecondition where is again the chirality vector and an integer. As a result, each band ofgraphenesplitsintoanumberof1-Dsubbandslabeledby

.Fig.2(b)shows thestatesofa(3,3) CNT.Thealloweden-ergystatesofthetubearecutsofthegraphenebandstructure.WhenthesecutspassthroughaFermipoint,asinthecaseof the (3,3) nanotube, the tube is metallic. In caseswherenocutpassesthroughaKpoint,thetubes aresemiconducting[Fig. 2(c)]. It can be shown that an (n,m) CNTismetallicwhen , it has a small gap (duetocurvature-inducedmixing)when [11], where is aninteger, whileCNTswith are truly semiconducting [8], [9].

As long as we restrict ourinterest to low energies (i.e., a few hundred meV from the Fermi energy) the band structure of a metallic nanotubecan be approximated by two sets of bands with a linear dispersion intersecting at and [see white lines in Fig. 2(b)]. Electrons with dE/dk 0 move to the right, while electrons with dE/dk 0 move to the left. In semiconducting CNTs the two bands do not cross at , but a diameter-dependent band gap develops with , where is the tube's diameter and the Fermi velocity [8], [9]. The above the- oretical predictions have been confirmed experimentally by scanning tunneling spectroscopy [12],[13].

The SWCNTs are 1-D objects and as such their two-ter- minal conductance is given by Landauer's equation: [14], [15] where is the quantum ofconductanceand is the transmission of a contributing conduction channel (subband). The sum involves all con- tributing conduction channels, i.e., channels whose energy lies between the electrochemical potentials of the left and right reservoirs to which the nanotube is connected. In the absence of any scattering, i.e.,whenall , the resis- tance ofametallicSWCNTis 6.5 k because, as wediscussedabove, 2. This quantum me- chanical resistance is a contact resistance arising from the mismatch of the number of conduction channels in the CNT and the macroscopic metalleads.

There is strong evidence that in the case of metallic SWCNTs, so that these tubes behave as ballistic conductors [16]–[19]. This arises from the 1-D confinement of the electrons which allows motion in only two directions. This constraint along with the requirements for energy and mo- mentum conservation severely reduces the phase space for scattering processes. However, in addition to the quantum mechanical contact resistance, there are other sources of contact resistance, such as those produced by the existence of metal-nanotube interface barriers, or poor coupling between the CNT and the leads. These types of resistance are very important and can dominate electrical transport in nanotubes, especially at low temperatures where typically they lead to charging and the observation of Coulomb blockade phenomena. Localization can also be induced by contacts to metallic electrodes, a fact that makes four-probe measurements very difficult, requiring special arrangements [19].

Unlike SWCNTs, the electrical properties of MWCNTs have received less attention. This is due to their complex structure; every carbon shell can have different electronic character and chirality, and the presence of shell–shell in- teractions [20], [21]. However, at low bias and temperatures, and when MWCNTs are side-bonded to metallicelectrodes, transport is dominated by outer-shell conduction [10], [22],

[23]. MWCNTs show 1-D or 2-D characteristics,depending on their diameter and the propertyconsidered.

III. FABRICATION AND PERFORMANCE OF CARBON NANO TUBEFETS

FETs, particularly in CMOS form, have been proven to be the most technologically useful device structures. It is, thus,naturalthat wehavechosentobuildsuchdevicesusing CNTs. The first such devices were fabricated in 1998 [24], [25].IntheseasingleSWCNT wasusedtobridgetwonoble metalelectrodesprefabricatedbylithographyonan oxidized silicon wafer as shown in Fig. 3. The SWCNT played the role of the "channel," while the two metal electrodes func- tioned as the "source" and "drain" electrodes.The heavily
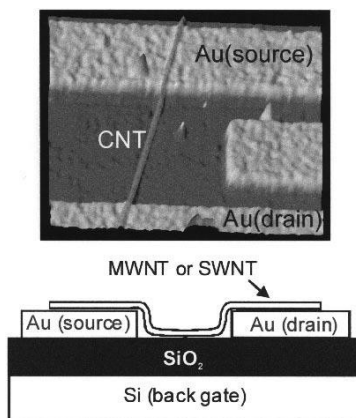

Fig. 3. Top: AFM image of one of our early CNTFETs. Bottom: Schematic cross section of the CNTFET [25].

dopedsiliconwaferitselfwasusedasthe"gate"(b ack-gate). These CNTFETs behaved as p-type FETs (we will return to this point in Section V) and had an I(on)/I(off) current ratio of 10 . While functional, the devices had a high para- sitic contact resistance 1M , low drive currents (a few nanoamperes),lowtransconductance 1 nS, and high inverse subthreshold slopes S 1–2 V/decade. To a large ex- tent the unsatisfactory characteristics were due to bad con- tacts. The

CNT was simply laid on the gold electrodes and washeldbyweakvanderWaalsforces.Toimprovet hecon- tactswe adapted a different fabrication scheme where the semiconducting SWCNTs (s-SWCNTs) were dispersed on an oxidized Si wafer, and the source and drain electrodes, now made of metals that are compatible with silicon tech- nologysuchasTiorCo,werefabricated ontopofthem[26]. Thermal annealing of the contacts, which in the case of Tielectrodes led to the formation of TiC, produced a stronger couplingbetweenthemetalandthenanotubeandare duction of the contact resistance [26],[27].

Fig. 4(a) and (b) shows the output andtransfercharacter-isticsof such a CNTFET with Co electrodes [26].Fromthe curves we see that the transistor is p-type andhas

a high on–off current ratioof 10 . ThisnewCNTFETconfiguration has a significantly reducedcontactresistance,30 k , a much higher current in the A range,andatransconductance 0.34 S,i.e., 200 timeshigher than that of van der Waals-bonded CNTFETs.

All of the early devices were back-gated with very thick gate insulators(SiOthickness 100-150 nm). As with conventional MOSFETs we should be able to improve their performance by increasing the gate capacitance by reducing the insulator thickness or increasing the dielectric constant. However, unlike in the MOSFET configuration where the capacitance is similar to that of a plane capacitor, i.e., gate capacitance, the CNTFET geometry will pre- dict a dependence [25]. In addition to increasing the gate capacitance, it is essential that each CNTFETisgatedindependentlybyitsowngatesoth atcom- plex integrated circuits can bebuilt.

A next generation of CNTFETs with top gates was fabri- cated by dispersing SWCNTs on an oxidized wafer. Atomic
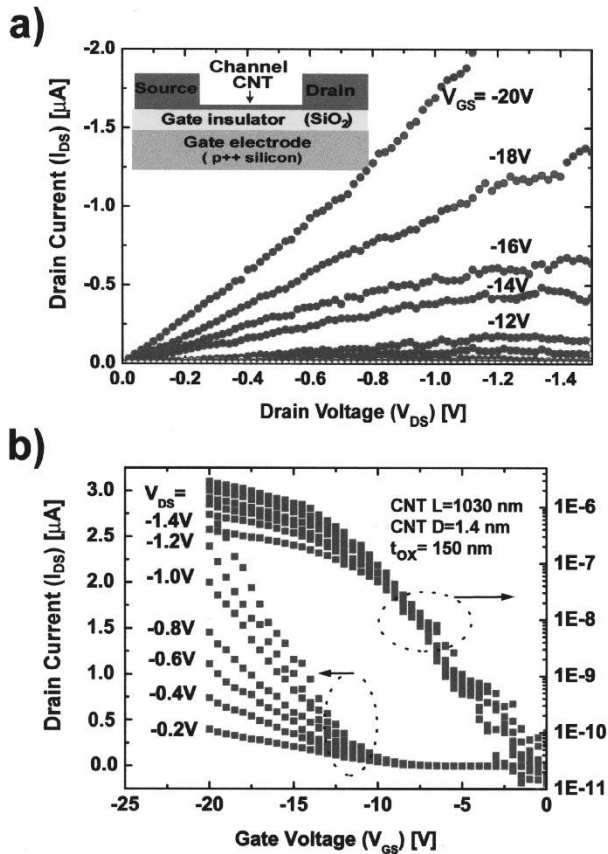
Fig. 4. (a) Output characteristics of a CNTFET with cobalt source and drain electrodes deposited on top of tube. (b) The corresponding transfer characteristics.

forcemicroscopy(AFM)imagingwasusedtoide ntifysingle CNTs,andtheTisourceanddrainelectrodeswerefa bricated on top of by e-beam lithography and liftoff [28]. After an- nealing at 850 C to transform the contacts into TiC[27],

a 15- to 20-nm-gate dielectric film was deposited by chem- icalvapor deposition (CVD) from a mixture of SiH and O at 300 C. Afterannealingfor 0.5 h at 600 C in N to densifytheoxide,50-nm-thickTiorAlgateelectrod eswere patterned by lithography andliftoff.

In Fig. 5(a) we show a schematic of a top-gated CNTFET, and in Fig. 5(b) the output characteristics of such a device with Ti electrodes and a 15 nm SiO gate insulator film

[28]. Such a CNTFET can also be switched by the bottom gate (wafer) and the resulting characteristics can be compared with those of the device under top-gate operation. This de-vicehasasuperiorperformance;thethresholdvolta geofthe top-gated CNTFET is significantly lower, 0.5 V, than under bottom-gated operation, 12 V. Similarly, the drive current ismuchhigherundertopgating,andthetransconduc tanceis similarlyhigh, 3.3 S pernanotube.

Since the eventual objective of nanotube electronics is tobe competitive with silicon electronics, it is important to compare their relative performances, despite the fact that the CNTFETs are still far from being optimized. In these experiments a single SWCNT is used, so we express the current carrying capabilities of the devices per unit width (per micrometer) as is the practice in microelectronics
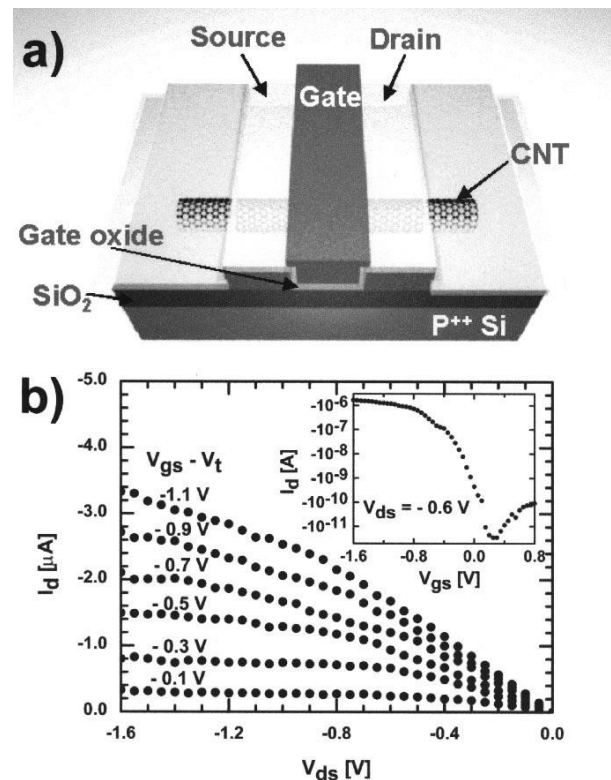

Fig. 5. (a) Schematic representation of one of our top-gated CNTFET with Ti source, drain, and gate electrodes. A 15-nm SiO film was used as the gate oxide. (b) The I–V characteristics of the device.

Table 1

Comparison of Key Performance Parameters for a 260 nm-Long Top Gate p-CNTFET, a 15-nm-Bulk Si p-MOSFET, and a 50- nm SOI p-MOSFET

diameterof the s-SWCNTs used was 1.4 nm. Table 1 shows the comparison of the characteristics of the CNTFET with two recent high-performance Si p-channel devices: a 15-nm-gate length MOSFET built on bulk silicon [29] and a 50-nm-gate length device built using SOI technology [30]. We also note that an optimal device layout may require the use of an array of CNTFETs. In this case the results can be scaled to give the total current for the array [26]. The current would increase the denser the packing of the tubes. However, screening at close separations can reduce the actual current per CNT by up to a factor of 2[31].

From Table 1 we see that the CNTFET is capable of de- livering three to four times higher drive currents than the Si MOSFETs at an overdrive of 1 V, and has about four times highertransconductance.Fromtheaboveandother consider- ations,itisclearthatCNTFETs,eveninthisearlysta geofde

	p-type CNTFET	Ref a	Ref b
Gate Length (nm)	260	15	50
Gate oxide thickness (nm)	15	1.4	1.5
V_t (V)	-0.5	~-0.1	~-0.2
I_{ON} (μA/μm) ($V_{DS} = V_{GS} - V_t \sim$ -1 V)	2,100	265	650
I_{OFF} (nA/μm)	-150	<-500	-9
Subthreshold slope (mV/dec)	130	~100	70
Transconductance (μS/μm)	2,321	975	650

a) B. Yu et al. IEDM Tech. Dig. 2001, p. 934; b) R. Chau et al. IEDM Tech. Dig. 2001, p. 621
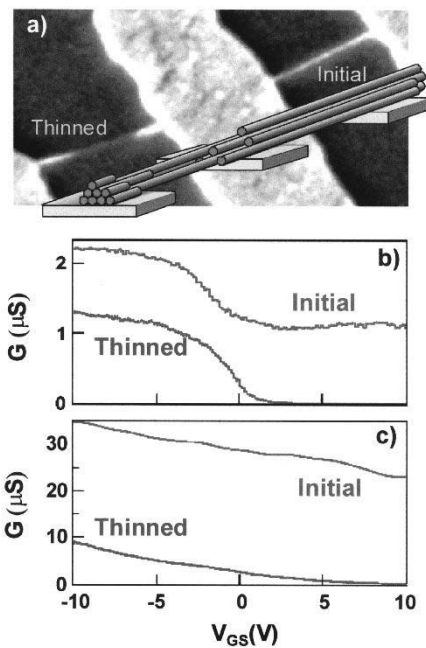

Fig. 6. Conductance (G) as a function of gate voltage (V) of a CNT bundle containing both metallic and semiconducting nanotubesbeforeandafterselectivebreakdownoft hemetallic

CNTs. (a) Images of the intact and thinned nanotube bundle. (b) G versus V fora thin bundle. (c) The same for a very thick bundle. Inthelattercase somesemiconductingtubeshadtobe sacrificedin order to remove the innermost metallic tubes in thebundle.

velopment, can be very competitive with the corresponding Sidevices.Furtherrefinementscanbeexpectedbya dditional reductions in and the use of high-insulators. We have already seen significant improvements by using HfOas a gate insulator [32], [52]. An insight to the ultimate potential of CNTFETs is provided by a recent study [33]. In this nan- otubeFET, the role of the gate was played by a droplet of an electrolyte connected to an electrochemical electrode. The combination of an electrolyte dielectric constant of about 80 and of the ultrathin (0.5 nm) Hemholtzlayer in the elec- trolyteledtoanextremelyhightransconductanceof about20

S. Further opportunities for improvements in the CNTFET performancearisefromnewinsightsontheswitchin gmech- anism in the CNTFET, as will be discussed in SectionV.

IV. TRANSISTORS FROM NANO TUBE BUNDLES: BUNDLE COMPOSITION ENGINEERING

A major impediment to the large-scale fabrication of CNTFETs is the fact that the current synthetic schemes for SWCNTs generate mixtures of metallic (m) and semicon- ducting (s) nanotubes. These tubes tend to adhere to each other, forming "bundles," or "ropes" [34]. No good methods exist for the preparation of only m- or s-CNTs by selective synthesis or postsynthesis separation. If CNTFETs were to be fabricated from such a bundle, the m-CNTs in thebundle would short out the device, as shown in Fig. 6. Currently, dilute suspensions of CNT bundles are ultrasonicatedand dispersed on a wafer. AFM imaging is then used to identify isolated CNTs to build the CNTFET. We have
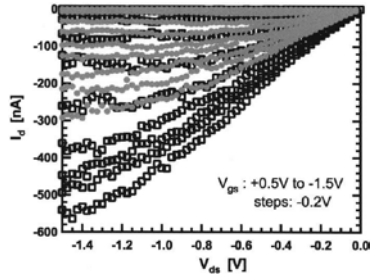
developed

Fig. 7. Drain current versus gate voltage curves of a CNTFET upon interchange of its source and drain [32], [52].

the technique of "constructive destruction" [20] that allows us to selectively destroy the m-CNTs in a rope, leaving the s-CNTs intact.

As we discussed earlier, CNTs can carry enormous cur- rent densities at low electron energies. At higher energies, however, optical phonon excitation is possible [35], [36]. This leads to current saturation and the deposition of large amountsofenergy,whicheventuallydestroystheC NTstruc- ture[36].Toapplythismethodtoremovem-CNTsfr ombun- dles, we first deposit the bundles on an oxidized Si wafer, then we fabricate on them an array of source drain and side gate electrodes. By applying an appropriate voltage bias to the gate, the s-CNTs can be depleted of their carriers. Then whenasufficientlyhighsource-drainbias isapplied,the generated current passes only through the m-CNTs, leading to their destruction, while leaving the s-CNTs essentiallyin- tact (see Fig. 6) [20]. In this way arrays of CNTFETs can be generated[20].

V.THE SWITCHING MECHANISM OF CARBON NANOTUBE TRANSISTORS

Up to this point we have implicitly assumed that the CNTFET switching mechanism is the same as that of conventional silicon devices. However, a number of obser- vations suggest otherwise. For example, Fig. 7showsthe versus curves for the same CNTFET upon interchange of the source and drain [32], [52]. A different current is obtained in the two cases. If the operation of the device were to be dictated by the properties of the bulk CNT, then the saturation current would be the same, since both sets of curves are taken with the same CNT. However, the different

characteristicscanbeaccountedforiftransportinth etubeis dominatedbybarriers(Schottkybarriers1)attheC NT–metal contacts.Inthatcaseasmallasymmetryofthebarrier satthe sourceanddrainjunctionscouldresultindifferentsa turation

1WeusethetermSchottkybarriersinitsmostgene ralsensetoaccountfor bandbendinginasemiconductoratametal/semicon ductorinterface.When arguing about the switching in CNT transistors, we assume that there is no additional barrier present in ourdevices.
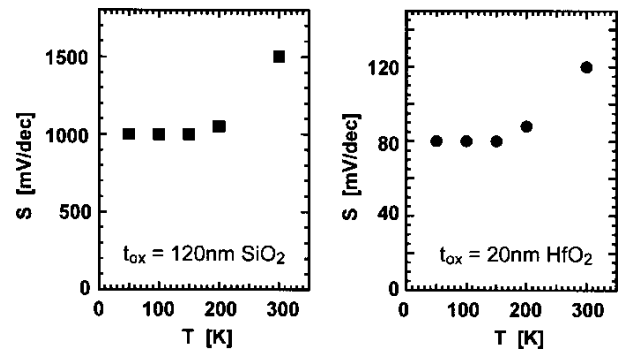

Fig. 8. Temperature dependence of the inverse subthreshold slopes, S, of two CNTFETs with 120 nm of SiO and 20 nm of HfO gate oxides, respectively [32], [52].

currents. Further support for the existence of these barriers comes from the study of the subthreshold characteristics of CNTFETs.

In long-channel FET devices, the drain current varies exponentially with , and for drain bias 3 k T/q it is essentially independent of [37]. A device char- acteristicof particular importance is the gate-voltage swing,orinversesubthresholdslopeS.Thisisgiven by

T/q .

For a fully depleted device, the depletion capacitance is zero; therefore, the second term in parenthesis becomes one. CNTs are aperfect example of adevice exhibiting 0, since no charge variation can occur across the tube circumference. Under these ideal conditions S depends only on the temperature and has a value of 60 mV/dec at 300 K. Deviations appear when

interface trap states are present in the oxide [37]. The capacitance due to these interface states is in parallel with the depletion capacitance. The early back-gated CNTFETs with thick (100–150 nm) gate oxides had unexpectantly high S values of 1–2 V/dec. Devices with thin oxides, such as the top-gated CNTFET in Fig. 5, have S 100–150 mV/dec. Interface traps could in principle account for these observations. However, we foundthatthehighSvaluesforthickoxidesareverys imilar independent of whether an n-type, a p-type, or an ambipolar transistor was measured. Since there is no doubt about the presence of Schottky barriers in case of an ambipolar device, and—as we proved [32], [52]—a Schottky barrier model alone can explain the trend of S as a function of quantitatively, interface traps are not responsible for the high S values in case of thick gate oxides. Further evidence that S is determined by Schottky barriers comes from its temperature dependence. As can be seen from Fig. 8, S is temperature dependent at higher temperatures but levels off at temperatures below about 200 K, suggesting a carrier tunneling process. The described subthreshold behavior maybe unexpected for a bulk-switched device, but can be fully accounted for by a Schottky barrier transistor model [32], [52]. Calculations of S as afunctionofbased on the SB and bulk models along with our own and literature experimental data are shown in Fig. 9. The data are fitted well by the SB model but not by the bulkswitchingmodel.
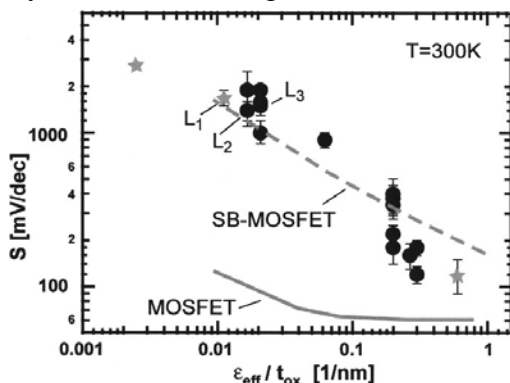

Fig. 9. Dependence of the inverse subthreshold slope S on the ratio " =t ,where" is the effective dielectric constant and t is the thickness of the gate oxide. The points areexperimental data fromour ownwork,aswellasfromtheliterature.Thesolidlin

eis thepredictedbehaviorforbulkswitching,whilethe dashedlineis thepredictionfortheSchottkybarrierswitching model[32],[52].

Focusing on the Schottky barrier itself, we note that the electrostatics in 1-D is different than that in 3-D and it is re- flected in the shape of the barriers [38]. In 1-D the barriers are thin, showing an initial sharp drop followed by a log- arithmically decreasing tail. Because of the thinness of the barrier, tunneling in 1-D is easy and can dominatetransport. In Fig.10(a)weshowtheschematicofatop-gatedCNT FET and the electric field generated by the gate in that structure. Fig. 10(b) gives the conductance of the device as a function ofthegatevoltagefordifferentvaluesoftheSchottk ybarrier height. Finally, Fig. 10(c) shows the source Schottky barrier for amid-gapCNTatthreedifferentgatevoltages[38]. The shape of the barrier and the thinning resulting from the gate field can be clearlyseen.

The SB model can also provide an explanation for the long-standing problem involving the effect of the ambient ontheperformanceofCNTFETs.Alreadyinthefirst studies of CNTFETs, it was observed that although the CNTs used were not intentionally doped, the fabricated CNTFETs were p-type [24], [25]. These early FETs were fabricated in air. It was later found that when CNTs are placed in vacuum, their electrical resistance increased and their thermopowerchanged sign [40]. It was proposed that the CNTs transfer electrons to atmospheric O and, thus, become doped with holes[41].

We have performed detailed studies of this gas effect on nanotubes in a CNTFET configuration [42]. In our early studies, we used a back-gated FET configuration with a thick (100–150 nm) gate oxide. As Fig. 11 shows, initially the air-exposed CNTFET was p-type. However,after an- nealing under vacuum becomes n-type. Furthermore, as Fig. 11 shows this unexpected transformation is reversible; reexposure to O brings back the p character of the FET. Intermediate stages where the CNTFET exemplifies am- bipolar behavior are clearlyseen.

The above findings prove that the p character of the CNTFETisnotanintrinsicpropertyoftheCNTs,but results

by annealing in vacuum into an n-type CNTFET and the reverse transformation upon exposure to O . The transformation proceeds viaambipolar intermediate states of the CNTFET. No threshold shifts are observed, and the drain currentatV = 0 does notchangefrom the interaction with O . We have performed a number of experiments to ascertain the nature of this interaction. In Fig. 12 we show the behavior of a CNTFET upon doping
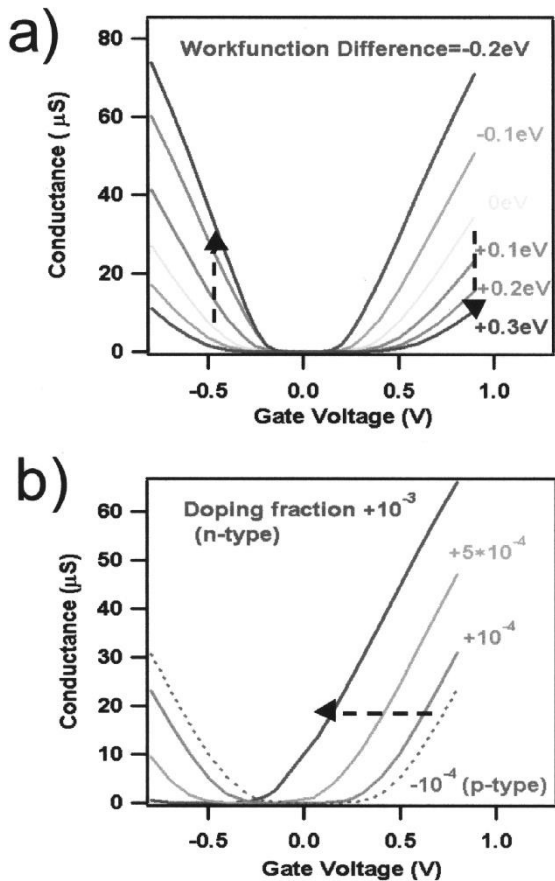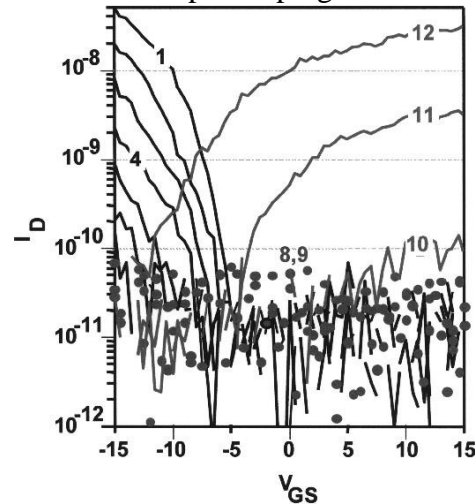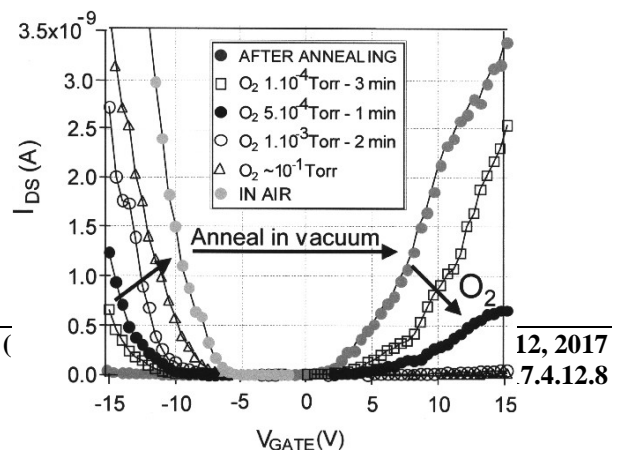

Fig. 12. The effect of doping with increasing amounts of potassium on the electrical characteristics of an initially p-type (curve 1) CNTFET.

Fig. 13. Qualitative diagram showing the lineup of the valence and conduction bands of a CNT with the metal Fermi level at the source–CNT junction first in air and after annealing in vacuum

with an electron donor, in this case potassium [42]. The well-known characteristics of doping, i.e., a shift of the threshold gate voltage and an increasing current at 0, are clearly seen. However, this behavior is in stark contrast with the behavior observed upon O exposure (see Fig. 11). From this and other experiments, we have concluded that although some doping by O may take place, this by itself cannot account for the observedbehavior.

Fig. 10. Simulation of the operation of a top-gated Schottky barrierCNTFET.(a)ThestructureoftheCNTFETa ndtheelectric fieldlines(V = 2 V).(b) Conductance versus gate voltage for different values of the Schottky barrier. (c) The effect of gate bias on the Schottky barrier at the source–CNT junction[39].

Fig. 11. Transformation of a p-type CNTFET

Aswehavealreadyshownabove,transportandswitching in CNTFETs is controlled by the Schottky barriers at the contacts. Oxygen then mustaffect these barriers. When a nanotube is bonded to a metal electrode the resulting charge transfer determines the lineup of the nanotube bands. However, this charge transfer and the resulting fieldcan be strongly affected by the coadsorptionof other species such as oxygen near or at the CNT–metal junction. These coadsorbatescanchangelocallythesurfacepotential[39]orFig. 14. Simulations of the effect of O and K on the CNTFETs current–voltage characteristics [39].

directly interact with the junction [43]. In Fig. 13 we give a schematicthataccountsqualitativelyforthebandlineupata metal–CNT junction in air and after annealing in a vacuum. The p character in air is the result of Fermi level pinning near the valence bandmaximum.

Support for this interpretation is provided by theoretical modeling. In order to take advantage of the simpler electro- statics, we used a model of a CNT surrounded by a cylin- drical gate. In Fig. 14 we simulate the I–V characteristics of a CNTFET upon oxygen adsorption by changing the local surfacepotential[39].Althoughthenumberscannotbecom- pared because of the different device geometry used in the calculation, it is clear that the resulting behavior is similar to that of Fig. 11. In contrast, a model where fixed charges are placed along the length of the tube in order to simulate a doping interaction gives a behavior similar to that of doping by potassium in Fig.12.

TheeffectofoxygendominatesthebehaviorofCNTFETs aslongasthegatefieldisweak.Thiswasthecaseforourear- lier structures with thick gate oxides. However, in ourrecent CNTFETs with thin oxides (2–5 nm), we observe am- bipolar characteristics even in air, indicating a near midgap lineup of the CNT bands[53]

VI. MULTIWALLED NANOTUBE FIELD-EFFECTTRANSISTORS

Our discussion above has been limited totransistors made out of SWCNTs. Low-temperature
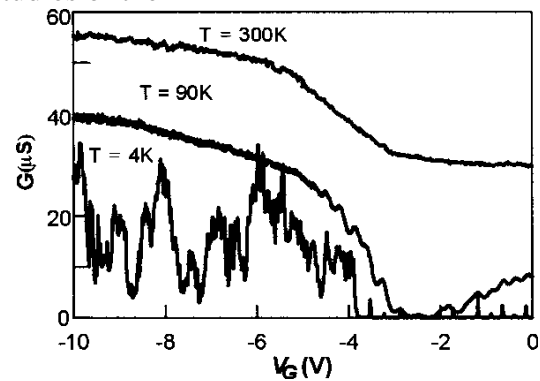
studies of the

Fig. 15. Temperature dependence of the conductance G of an MWCNT as a function of the gate voltage.

Aharonov–BohmeffectinMWCNTshaveconcludedthatin MWCNTs side-bonded to metal electrodes, effectively only the outer shell contributes to electrical transport [22]. One would expect then that MWCNTs with a semiconducting outer shell could be used to fabricate CNTFETs. However, in semiconducting CNTs, thebandgap is inversely proportional to the tube diameter; therefore, only small-di- ameter MWCNTs are expected to display large switching ratios at roomtemperature.

In Fig. 15 weshow the effectof the gate voltage on the conductance G of a 14-nm diameter MWCNT, at dif- ferent temperatures [21]. Clearly, the gate can modulate the conductance of the MWCNT channel at room temperature. However,thereisalargeresidualconductance,whichcanbe assignedtothecouplingoftheouter semiconductingshellto an inner metallic shell. This coupling is expected to be acti- vated with an activation energy of the order of 2. At low temperatures, the contribution of the inner metallic shell is suppressed (see Fig. 15). These observations indi- cate that the transport characteristics of an MWCNT at am- bienttemperaturemayhavecontributionsfrommorethanthe outer shell even for side-bonded CNTs. Because of the ac- tivated nature of the shell-to-shell transport, and given that thesemiconductinggapisinverselyproportionaltotheCNT diameter, multishell transport should be more important for large-diametertubes.

When the applied is increased, the average

energyofthe carriers is expected to increase, as well as the coupling

between the carbon shells. As we discussed in Section IV, higherelectronenergiesleadtoenergydissipationandbreak- down. Our studies of MWCNTs have shown that initiation of the breakdown occurs at a power threshold, which is sig- nificantly lower in air than in vacuum [36]. This indicates that an "oxidation" process takes place in air. The oxida- tion is most likely not a purely thermal process. Calcula- tionson graphite have shown that once certain defects are generated,e.g.,di-vacancies,aself-sustainingchainreaction withoxygencantakeplace[44].Becauseofthelowerbreak- down threshold in air, the shell breakdown in MWCNT pro- ceeds sequentially from the outer to the inner shells. This shell-by-shellbreakdowncanbeseenasastepwisedecrease inthecurrent flowingthroughtheCNT[seeFig.16(a)].Itis also illustrated by AFM images of an MWCNT drapedover
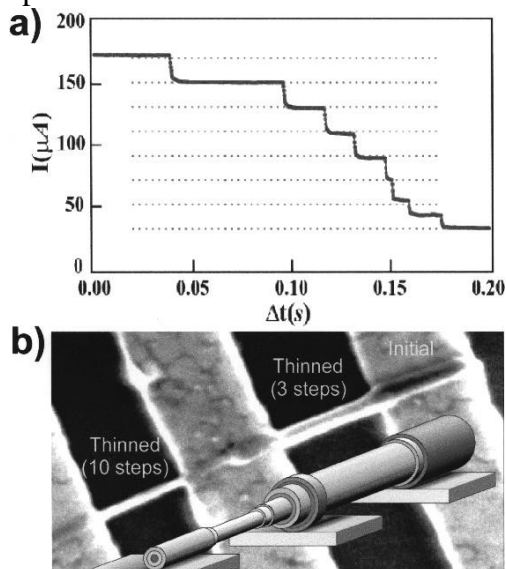

Fig. 16. (a) Stepwise decrease of the current during the breakdown of an MWCNT. (b) Images of an MWCNT showing part of the initial tube, as well as segments of the same MWCNT from which three and ten carbon atom shells have been removed.

several metal electrodes, so that individual CNT segments canbeelectricallystressedindependently.Thinned segments that have lost three and ten shells, respectively, as well as a portion of the initial

MWCNT, are clearly seen [Fig. 16(b)]. Thecapabilitytoremovecarbonatom shellsonebyoneand identify their character through the effect of the gate field [20], [21], along with the diameter dependence of the band gap 1 allows the fabrication of CNTFETs withadesired can be fabricated using the controlled breakdownprocess.

VII. CARBON NANOTUBE INTEGRATEDCIRCUITS: LOGICGATES

So far we have concentrated our discussion on the performance of individual CNTFETs. The fabrication of integrated circuits using such devices is the next step. In 2001 we demonstrated that this was possible by fabricating a CMOS-like voltage inverter (a logic NOT gate) [45]. For simplicity, we used the early design of CNTFETs involving the CNT on top of gold electrodes

In Fig. 17 we show the structure and electrical charac- teristics of an inverter circuit involving a n- and a p-CNT- FETs. Originally, both CNTFETs were p-type because of their exposure to air (oxygen). We then covered one ofthem by a protective film of PMMA (a more stable protection is provided by a SiO film [27]), while the other was left un- protected. Both of the CNTFETs were then annealed under vacuum, which transformed both of them into n-type. After cooling, the pair was exposed to oxygen, which converted the unprotected CNTFET to p-type, while the protected one remained n-type. In this way, the two complementary CNT- FETs needed were formed and wired.

The inverter works the same way as an ordinary CMOS inverter. The input voltage is applied simultaneously to the gates of the complementary CNFETs. The p-CNFET is poFig. 17. (a) Schematic representation of the internanotube voltage inverter (NOT gate). One of the FETs is protected by a layer of PMMA. (b) After annealing two p-CNTFETs in vacuum to form two n-type CNTFETs. (c) After exposure to oxygen at 300 K.

(c) Electrical behavior of theinverter. larizedbyapositivevoltage,then-FETbyanegative voltage, andacommoncontactisusedastheintermolecularinverter's

output.Apositiveinputvoltageturnsthen-CNFET" on"(the p-CNFET being "off"), resulting in the transmission of the negativevoltagetotheoutput.Anegativeinput,onth eother hand, turns the p-CNFET "on," producing a positiveoutput. The electrical characteristics of the CNTFETs at each stage and those of the resulting inverter are shown in Fig. 17. We refer tothisinvertercircuitasanintermolecularinverterb e- cause it involves two nanotubemolecules.

Ideally,onewouldliketoachievetheultimateleve lofinte- grationbyfabricatingthecircuitsalongthelengthof asingle CNT, i.e., form an intramolecular circuit. A first realization of this approach is shown in Fig. 18(a) [44]. As the AFM image shows, the nanotube is placed on top of three prefab- ricated gold electrodes. In this way two back-gated initially p-typeCNTFETsareformed.Thentheyarebothcov eredby PMMAandawindowisopenedbye-beamlithograp hyover thechannelofoneofthem.Throughthiswindow,the channel isn-dopedusingpotassiumasadopant.Inthiswaytw ocom- plementary FETs are formed along the same nanotube. The electrical characteristics of the resulting inverter are shown inFig.18(b).Itisparticularlyinterestingthatdespite thefact thatnoeffortwasmadetooptimizetheconstructiona ndper- formance of the individual CNTFETs, the resulting inverter hadagainofalmosttwo.Thissuggeststhatoptimize dCNT- FETswouldleadtomuchhighergainandcanbewire dalong thelengthofasingleCNTtoproducemorecomplexc ircuits. Following this initial work [45], more nanotube logic gates of complementary [46] or transistor–resistor [47] type have beendemonstrated.
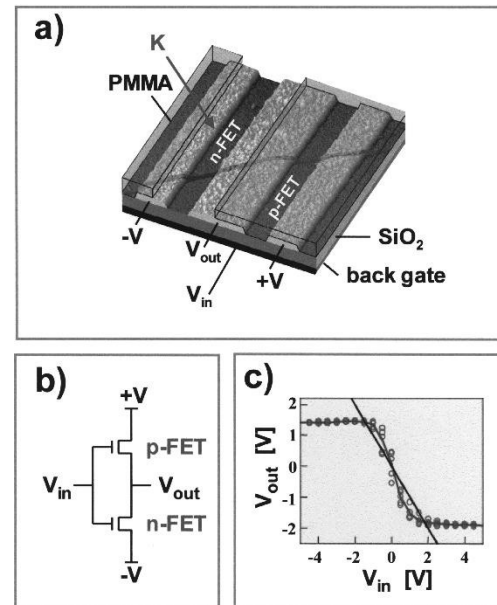

Fig. 18. (a) Atomic force microscope image of the intrananotube voltage inverter. (b) Schematic of the inverter. (c) Electrical behavior of the intrananotube inverter.

VIII. NANOTUBESYNTHESIS

SWCNTs are produced using arc discharges [2], [3],laser ablation of a carbon target [34], or CVD [48]. In all of these techniques, a metal catalyst (typically Co, Fe, and/or Ni) in the form of nanoparticles isutilized.

Currently, catalytic CVD is the most widely used tech- nique [48]. One of the advantages of this approach is that it allows nanotubes to be grown locally by placing the catalyst at the appropriate location [49]. We have experimented with catalytic CVD using a combination of electrolytic and litho- graphic approaches to control both the location and orienta- tionof the growth. The procedure shown in Fig. 19 involves the following steps:

1) patterning a thin, heavily doped silicon surface layer lithographically;

2) electrolytically etching the silicon to form porous sil- icon on the sidewalls of the patternedstructure;

3) protecting with photoresist the areas of the siliconsur- face where we do not want CNTgrowth;

4) driving into the exposed pores the metal catalyst, and

afterremovingtherestofthephotoresist,reactingwith CH at 1000 C to formSWCNTs.

Fig. 20 shows SEM images of SWCNTs grown this way bridging adjacent silicon pads. These pads can subsequently be metallized.

Quite often, the presence of heavy metal catalyst parti- cles in the nanotube product is unwanted but their removal is problematic and usually leads to damaged nanotubes. In applications in nanoelectronics, it is also likely that arrays of parallel oriented tubes will be needed in order to reduce the impedance of the devices and provide a high drive cur- rent [26]. Oriented growth of tubes is a very desirable way to achieve this type of nanotube organization. Postsynthesis alignment has also been pursued [50].
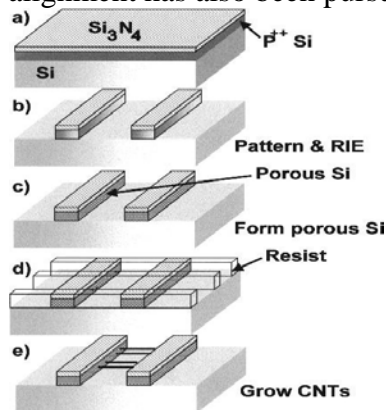

Fig.19.Sequenceoflithographicandother processingstepsused to produce selective local growth of SWCNTs by chemical vapor deposition using CH as the source ofcarbon.
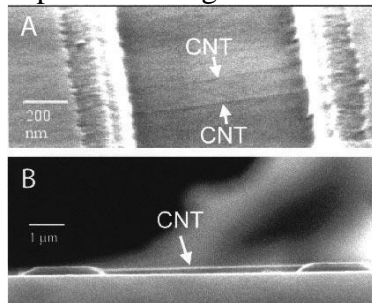

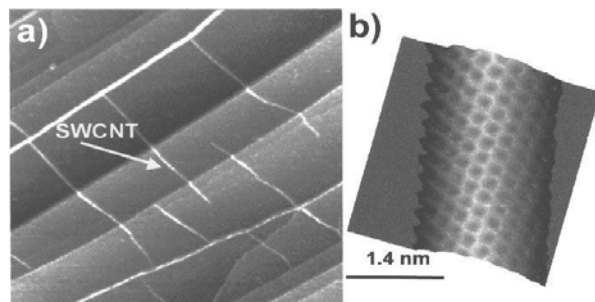Fig. 20. Electron microscope images (top and side views) showing locally grown CNTs connecting silicon electrodes

Fig. 21. (a) STM image of oriented (parallel) SWCNTs produced by heating under high vacuum to 1650 C a 6 H-SiC wafer with a (0001) Si-face. (b) Atomic resolution STM image of a SWCNT produced by this method.

Recently, we discovered a way to produce oriented SWCNTs by a catalyst-free approach [51]. This approach involves the thermal annealing under vacuum of SiCcrys- tals. Specifically, 6H–SiC wafers with a polished (0001) Si face (this surface is equivalent to the (111) surface of cubic SiC (3 C–SiC)) were heated to 1650 C at 10 torr.

Fig. 21(a) shows a scanning tunneling microscope (STM) image of a sample cut along the (1, 1,0,0) axis of the wafer resulting in a morphology characterized by well-ordered parallel steps in the (1,1, 2,0) direction. The white 1-D structures, identified as the CNTs, extend over several steps or terraces and are not presenton the samples annealed in vacuum at a temperature below 1400 C. An atomic resolution image of a semiconducting nanotube is shown in Fig. 21(b). From such images, as well as TEM images, the diameter of the nanotubes produced was determined to bein the range of 1.2–1.6 nm. These tubes are seen to have their axis perpendicular to the surface steps or be aligned along the steps. Extensive STM and AFM studies showed that this organization is uniform over their entire area of the sample. When the surface morphology is composed of terraces, the nanotubes form a weblike network with a predominance of 120 angles between straight sections (not shown)[51].

AlongwithindividualSWCNTs,thickertubesareal soob- served. Manipulation experiments using the tip of anAFM

[51] indicate that these structures are SWCNT bundles, not MWCNTs.

The orientation of the nanotubes could be a result of the growth process or may involve a postsynthesis rearrange- ment. Our AFM experiments show that the tubes are mo- bile on the surface at the high temperature used for their formation. This is deduced by the observation that after per- turbingthestructureofthenanotubesbyAFMmanipulation, annealing at a temperature of 1300 C, i.e., at a tempera- turelower than that needed for nanotube formation, brings the manipulated nanotubes back to their parallel orientation.

Thus, we believe that the orientation of the nanotubes re- sultsfrom their motion that releases part of the mechanical stress incorporated in the randomly grown network by fa- voring straight segments and by matching their orientation to the crystallographic structure of the surface. At the same time,formationofbundlescontributestoloweri ngofthe totalenergy.

The above findings suggest that: 1) it may be possible to

orient preformed nanotubes on an inert substrate by heating them at a temperature at which they acquire sufficient mo- bility and 2) in principle, it is possible to synthesize nan- otubes in a controlled manner by patterning graphene strips followed by annealing. By selecting the direction of the cut of the strip, the chirality of the resulting nanotube can be chosen.

CONCLUSION AND THEFUTURE

CNTs are new materials with outstanding electrical properties. The high conductivity and exceptional stability of metallic nanotubes makes them excellent candidates for futureuseasinterconnectsinnanodevicesandcircui ts.FETs using semiconducting CNTs have operating characteristics that are as good as or better than state-of-the-art silicon devices, and significant improvements should be expected in the near future. However, while CNTs are one of the most promising materials for molecular electronics, many challenges remain before they can become a successful technology. Most challenging are the materials issues. We still lack a method that produces a single type of CNT.In this respect, seeded growth techniques are a possibility and need to be explored. Another possible solutioninvolves the development of efficient separation techniques, and work is pursued in this direction with encouraging initial results. The sensitivity of the electrical properties of CNTs and CNT devices to the nature of the CNT–metal contacts and the ambient environment demonstrated in this article shows that better understanding and control of these problems is absolutely essential. For CNT device integration, new fabri- cation techniques that are based on self-assembly of CNTs are highly desirable. While our own current interest is in computer electronics, it is likely that the initial applications of CNT devices will be in less integrated systems such as sensors, or in special applications where devices of excep- tional miniaturization and performance are needed. Apart from their technological importance, CNTs are ideal model systems for the study and understanding of transport in 1-D systems and for the development of molecular fabrication technologies.

REFERENCES
[1] S. Iijima,"Helical microtubules of graphitic carbon," Nature, vol. 354, pp. 56–58,1991.
[2]S.IijimaandT.Ichihashi,"Single-shellcarbonnanot ubesof1nm diameter," Nature, vol. 363, pp. 603–605,1993.
[3]D.S.Bethune,C.H.Kiang,M.S.Devries,G.Gorman, R.Savoy,
J. Vaszquez, and R. Beyers, "Cobalt-catalyzed growth of carbon nanotubes with single atomic layer walls," Nature, vol. 363, pp. 605–607, 1993.
[4] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, Eds., Carbon Nanotubes: Synthesis, Structure Properties and Applications. Berlin, Germany: Springer-Verlag,2001.
[5] P. L. McEuen, M. S. Fuhrer, and H. Park, "Single-walled carbon nanotubeelectronics,"IEEETrans.Nanotechnol.,vol.1 ,pp.78–85, Mar.2002.
[6] C. Dekker, "Carbon nanotubes as molecular quantum wires," Phys. Today, vol. 52, p. 22,1999.
[7]P.G.CollinsandP.Avouris,"Nanotubesforelectroni cs,"Sci.Amer., vol. 283, pp. 38–45,2000.
[8] M. S. Dresselhaus, G. Dresselhaus, and R. Saito, "Carbon fibers based on C and their symmetry," Phys. Rev. B, vol. 45, pp.6234– 6242,1992.
[9]J.W.Mintmire,B.I.Dunlap,andC.T.White,"Arefull erenetubules metallic?," Phys. Rev. Lett., vol. 68, pp. 631–634,1992.
[10]S.Frank,P.Poncharal,Z.L.Wang,andW.A.deHeer ,"Carbonnan- otubequantumresistors,"Science,vol. 280,pp.1744–1746,1998.
[11]M. Ouyang, J.-L. Huang, C. L. Cheung, and C. M. Lieber, "En- ergy gaps in 'metallic' single-walled carbon nanotubes," Science, vol. 292, pp. 702–705,2001.
[12]J.W.Wildoer,L.C.Venema,A.G.Rinzler,R.E.Sma lley,and
C.Dekker,"Electronicstructureofatomically-resolved carbonnan- otubes," Nature, vol. 391, pp. 59–62,2001.
[13] T.W.Odom,J.L.Huang,P.Kim,andC. M.Lieber,"Atomicstruc- ture and electronic properties of single-walled nanotubes," Nature, vol. 391, pp. 62–64,2001.
[14]Y.ImryandR.Landauer,"Conductanceviewedastr ansmission,"Rev. Mod. Phys., vol. 71, pp. S306–S312, 1999.