

Adsorption of noble gases on individual suspended single-walled carbon nanotubes

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Abstract

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Physics

I. Abstract

The focus of this work is a study of the adsorption of noble gases on individual, suspended, single-walled carbon nanotubes (SWNTs). The surface of a SWNT is a cylindrical cousin of graphite, but the binding energy is smaller and the cylindrical geometry and lack of grain boundaries could be expected to lead to substantially different behavior. The coverage (areal density) on a nanotube can be measured with high precision from the mechanical resonance frequency shifts, yielding isotherms as a function of gas pressure analogous to volumetric isotherms on bulk substrates. The electrical conductance of the nanotubes can also be measured at the same time and the effects of the adsorbates on the conductance thereby investigated.

We found that adsorbed noble gases form monolayers on SWNTs, analogous to those on conventional 2-dimensional (2D) substrates, with a variety of 2D phases as a result of atom-atom interactions. Based on a combination of the coverage and conductance isotherms, the behavior of the adsorbates on SWNTs

was established, including the 2D phases, 2D critical and triple-point temperatures, binding energies, isosteric heats, and latent heats.

The majority of measurements were on Ar and Kr, fewer on ^4He and Xe. The binding energy, ε_0 , of the noble gases on a SWNT was found to be lower than on graphite, as anticipated. For example, ε_0 for Ar on one device was about $725 \text{ K} \pm 50 \text{ K}$, about 30% lower than graphite. The lower binding energy allows isotherm measurements at lower temperatures compared because the required pressure are higher. In all cases we found that only a single atomic layer is formed before reaching the saturated vapor pressure of the adsorbate.

Remarkably, although the binding energies of Ar were consistent between multiple SWNTs, the adsorbates on different devices did not behave in the same way. The device can be classified into two classes. Those in Class I show sharp first-order transitions between 2D phases, very similar to those on graphite, and the maximum monolayer coverage on SWNTs is consistent with that on graphite taking into account the radius of nanotube. Large and sharp risers at constant pressures in the coverage or conductance isotherms indicate the 2D liquid-vapor or commensurate solid-vapor conversion. Small and smoother risers following the large ones in the isotherms indicate the 2D incommensurate solid-liquid phase transitions. In contrast, devices in Class II do not show clear phase transitions, have non-vertical isotherms in regions where first-order jumps would be expected, and the monolayers seem to be not complete when the saturated vapor pressure is reached. The difference in isosteric heat between devices of the two classes within the region where the first-order transition is expected, may be due to the 2D L-V latent heat. The existence of the two different classes of behavior remains puzzling. It appears that in class II nanotubes the effects of atom-atom attractive interactions are suppressed, due possibly either to geometrical effects or the different electrical properties of different nanotube species.

II. Acknowledgements

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I want to say thank you to my parents for their understanding and support for whatever I do. It is lucky to be their child.

Finally, I would like to call this thesis a gift to Candy and Hat. They are my sister and brother forever.

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Chapter 1. Introduction

We start with the background of physical adsorption and binding energy, introduce 2D phase transitions of Ar, Kr, Xe and ^4He on graphite, discuss the properties of single-walled carbon nanotubes, and finally describe some previous work of the vibration resonance of carbon nanotubes and adsorption effects on the conductance of devices. Finally, we finish this Chapter with a summary of Z. Wang's results, which preceded the work done in this thesis.

1.1 Physical Adsorption and Binding Energy

Studies of adsorption of simple atoms and molecules (the adsorbate) on different substrates (the adsorber) have been done for a long time (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19). Depending on the strength of the substrate attraction relative to the adsorbate-adsorbate interaction, atomic/molecular layers may be formed. For strong adsorbents, like basal plane graphite, layer by layer growth has been observed, especially in studies with Kr, Ar, H_2 , CH_4 , etc. using adsorption isotherms, ellipsometry, calorimetry and neutron and X-ray scattering on exfoliated or single crystal samples (20) (7) (11) (21) (22).

At the other extreme, for very weak binding substrates (such as alkali metals), not even a single atomic layer can be formed before forming a 3d crystal. The intermediate case of conducting metals like Ag and Au has also been studied extensively, especially using quartz microbalance and surface plasmon resonance techniques. Here usually one observes triple point wetting. At T much lower than the triple point only one layer is formed, but as T -triple is approached more layers can be formed.

Carbon nanotube bundles have essentially two relatively well defined sites, the grooves between adjacent nanotubes and the outside surface of the nanotube. The grooves have larger binding energy sites than (1000) graphite, while the outside bundle surface offers a weaker binding site. Unfortunately truly homogeneous bundles do not exist, thus results usually show two broad distributions of binding energies, plus other heterogeneous sites.

Individual single-walled carbon nanotubes offer the possibility of a range of binding energies: the tube graphene is only one atomic layer thick (leading to lower binding than on graphite), and the various diameters of the nanotubes should lead to a possible variation in the total binding energy. A pristine nanotube is amenable to theoretical modeling, thus comparison between theory and experiment is possible (23) (24).

We will present results of extensive studies of the adsorption of Ar and Kr on single-walled carbon nanotubes to measure their binding energy on this novel substrate. We use resonance and conductance techniques to measure monolayer adsorption. All measurements have been done in the range where 2d phase transitions are known to occur for the same adsorbates on graphite. The weak binding produces higher equilibrium vapor pressures for isotherms at the same temperature on a nanotube than on graphite, allowing us to extend the measurements to considerably lower temperatures than reported in the graphite adsorption literature. We briefly describe our techniques, present the data, calculate binding energies from the data, and compare to existing calculations where possible.

1.2. Phases of Ar, Kr, Xe and ^4He on graphite

Ideally, rare gases forming a monolayer of atoms will behave like interacting substances in two dimensions (2d). On finite size smooth substrates, one expects to find gas or vapor (V), liquid (L) and solid (S) phases, with regions of coexistence between two phases, a 2d liquid-vapor critical point and a 2d solid-liquid-vapor triple point. With adsorbed films, the substrate plays a substantial role, and new phases may appear. This is the case with Kr and ^4He where a commensurate phase is formed by the atoms on the surface of graphite. On the other hand, Ar has a phase diagram rather similar to what one would expect for a Van der Waals gas but with some notable differences. From extensive measurements on different substrates we should expect that the 2d L-V critical point will occur at about 0.39 of $T_c(3d)$, while the 2d triple point will occur at about 0.6 of $T_t(3d)$. Variations from these rules occur due to the substrate. Here we summarize the phases of the four gases we studied when adsorbed on graphite. For an extensive description, see Bruch, Cole and Zaremba (17).

Ar

Ar on graphite has a conventional 2d Van der Waals phase diagram, with a liquid-vapor critical temperature, $T_c(2d) \sim 54 \text{ K} \sim 0.4T_c(3d)$ and a solid-liquid-vapor triple point, $T_t(2d) \sim 48.5 \text{ K} \sim 0.6T_t(3d)$ (25). The heat capacity measurements however show that most of the ordering (maximum heat capacity or largest change in entropy) occurs between the critical and triple point temperatures. The heat capacity signal at the triple point is sharp but rather small in magnitude. This indicates that considerable ordering already occurs in the liquid. (25)

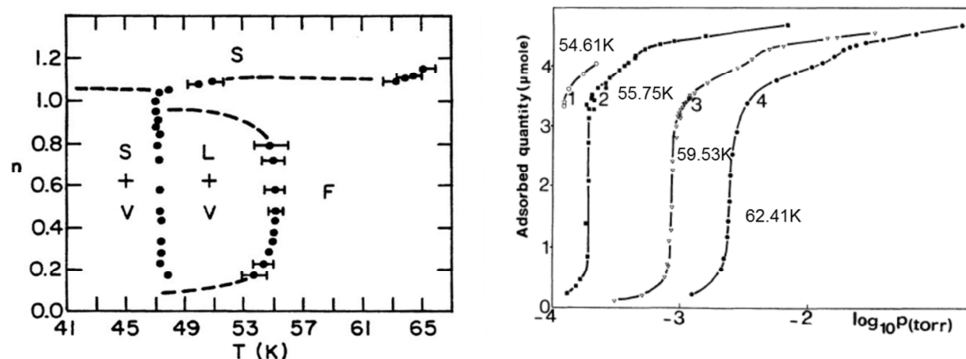


Figure 1.1 (a) Phase diagram of Ar adsorbed on graphite surface obtained from heat capacity measurements - V, L, F, and S mean vapor, liquid, fluid, and solid respectively (25).

Figure 1.1 (b) Isotherms for Ar on graphite – The temperatures are, 54.61, 55.75, 59.53, and 62.41 K. (26)

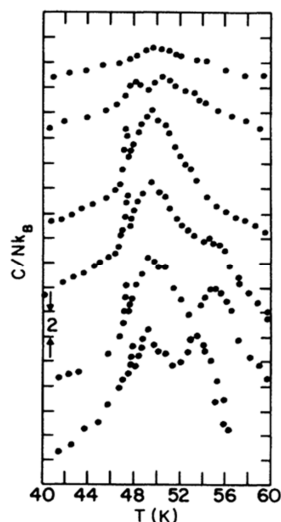


Figure 1.1 (c) - Heat-capacity scans of Ar on graphite at coverages (from bottom to top) $n = 0.175, 0.572, 0.717, 0.872, 1.043$, and 1.068 – Adopted from Migone et al. (25)

Kr

Kr adsorbed on graphite does not have a conventional 2d phase diagram because it forms a commensurate structure on it, pre-empting the liquid-vapor condensation. The Kr-Kr potential interaction minimum is slightly smaller than the distance at which one Kr atom sits on six carbon atoms [Fain, Suzanne, Sutter].

Ostlund and Berker calculated multicritical phase diagrams for krypton submonolayers adsorbed on graphite, see Fig. 1.2 (a). The theoretical result agrees with experiments quantitatively, as shown in Fig. 1.2 (b). (27)

Thomy and Duvall were the first to measure adsorption isotherms from $T = 77.4\text{K}$ up (28). Whether there was, or not, a small liquid-vapor coexistence region at low densities was further explored by Larher (29). These measurements were the first to show the very high surface quality of exfoliated graphite and paved the way for Low Energy Electron Diffraction (LEED) studies of this system that showed the formation of a commensurate structure (CS), one Kr atom per six C atoms, or coverage $\phi = 1/6$. It is possible to compress the Kr atoms out of the CS, to form an incommensurate solid structure (IS) rotated with respect to the orientation of the graphite planes. Heat capacity measurements by Butler et al. (30) outlined the phase diagram boundaries below the CS density, Fig. 1.2 (c). Further studies using X-ray diffraction at higher temperatures completed the first layer diagram (see Bruch, Cole and Zaremba, Fig. 6.12) (17).

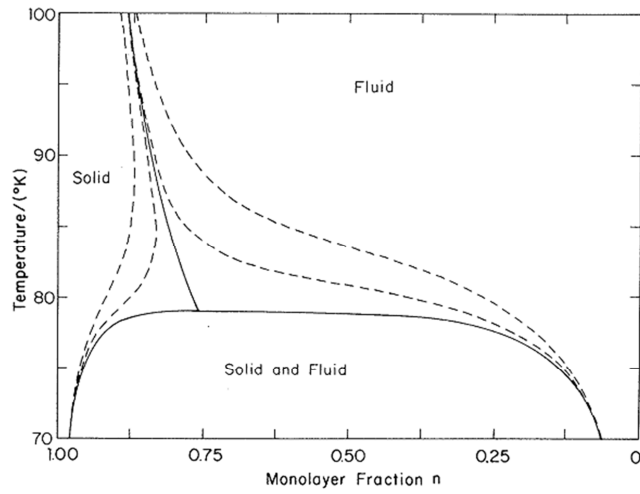


Figure 1.2 (a) - Predicted phase diagram on the multicritical region for krypton on graphite – Full curves presents the ideal thermodynamic system ($\Delta T = 0$ K). Dashed curves correspond to results of temperature smearings $\Delta T = 0.1$ K and 0.8 K. (27)

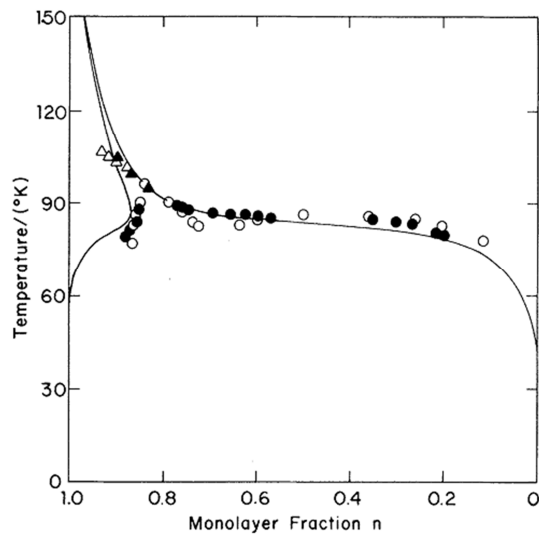


Figure 1.2 (b) – Predicted phase diagram for krypton on graphite, smearing $\Delta T = 0.8$ K, (27) compared with experimental data – First order transitions: open circles from Ref. (31), and closed circles from Ref. (32). Higher order transitions: open triangles from Ref. (31), and closed triangles from Refs. (33) (34) (35).

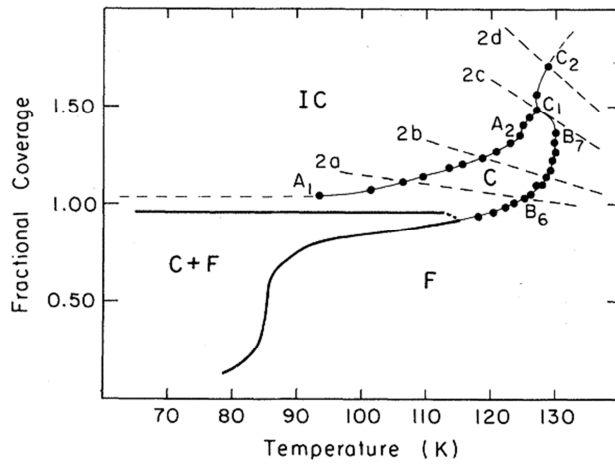


Figure 1.2 (b) - The low density phases of Kr adsorbed on graphite - At higher coverage this system is quite complicated with liquid and incommensurate solid phases. Here F represents fluid, C represents commensurate solid, and IC represents incommensurate solid. (17) (36)

Xe

Density-temperature phase diagram derived from adsorption isotherms and heat capacity measurements shows that the S-L-V $T_t = 99$ K, and the L-V $T_c = 117$ K (28). With addition of a second layer, the IS Xe will compress into a first layer CS structure. This is sufficient to discuss my results on Xe/nanotube.

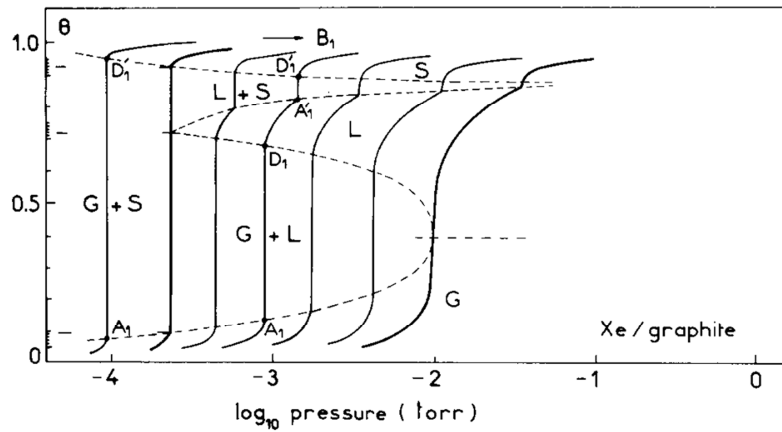


Figure 1.3 - The evolution of Xe adsorption isotherms between 97 and 117 K on a homogeneous graphite surface – Here G represents gas, L represents liquid, and S represents solid. (28)

⁴He

⁴He and ³He adsorbed on graphite or carbon nanotube bundles have been in great interests (1) (37) (38). Study of the He adsorbates may be illustrative to quantum issues (39) (40), and interestingly, ⁴He and ³He adsorbed on graphite can have commensurate solid state (41) (42) (17).

All phase transitions of ⁴He on graphite occur at temperatures below 4.2K, except for the possibility of observing its two dimensional melting line above this temperature and near monolayer completion (Bretz et al., Elgin and Goodstein). The cryogenic system used for my adsorption studies cooled down to about 4.2K, so I will not discuss the possible phases that occur below this T.

As a note, besides ⁴He and ³He, small molecules, H₂, HD, and D₂ adsorbed on graphite also show quantum effects (1) (17) (43). Para-H₂ monolayers on graphite show commensurate-solid state, like He, in heat-capacity measurements (44). Ne, the rare gas has mass between ⁴He and Ar, provides a link between the low mass atoms/molecules and heavier noble atoms (45) (46). But, we are not going to discuss them here.

1.3. Properties of single-walled carbon nanotube

A single-walled carbon nanotube (SWNT) is a pristine curved sheet of graphene where quasi two-dimensional phases of adsorbed matter can be observed. The properties of a SWNT depend on the properties of graphene and how the graphene sheet is rolled up.

The cylindrical shape of a SWNT, the rolled up sheet of graphene, provides a boundary condition on the electron wave function in the circular direction, and limits the allowed states to equidistance lines in k-space. One defines a roll-up vector with indexes (n_1 , n_2) to specify the curvature and chirality of a SWNT as shown in Fig 1.4 (a). Chirality is defined as the angle between the orientation of the lattice and the SWNT's axis.

The armchair carbon nanotubes, $n_1 = n_2$, have the chiral angle = 30°, shown in Fig. 1.4 (b). SWNTs with chirality 0°, i.e. $n_2 = 0$, are called zigzag SWNTs, see Fig. 1.4 (c).

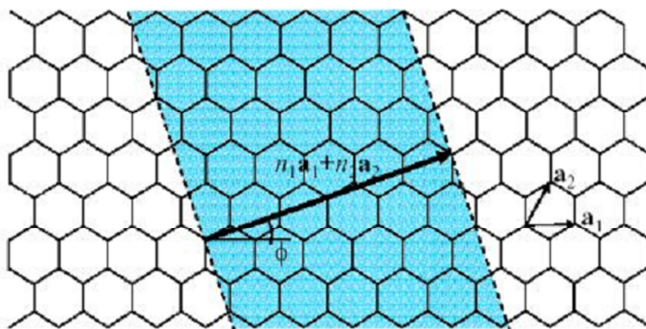


Figure 1.4 (a) – Forming a single-walled carbon nanotube from a graphene sheet, adopted from Minot and Sazonova – The graphene lattice vectors are $\mathbf{a}_1$ and $\mathbf{a}_2$. The shaded area shows the part of the sheet to be wrapped and the black arrow identifies the direction of wrapping, $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 = 4\mathbf{a}_1 + 2\mathbf{a}_2$. The “chiral” angle is the angle between the direction of wrapping and the lattice vector $\mathbf{a}_1$. (47) (48)

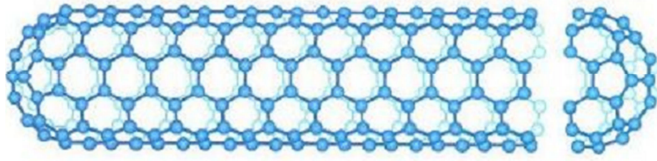


Figure 1.4 (b) – An “armchair” CNT (chiral angle = 30°) adopted from Sazonova (48)

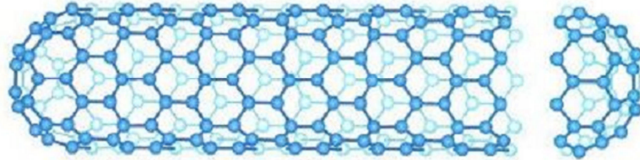


Figure 1.4 (c) – A “zigzag” CNT (chiral angle = 0°) adopted from Sazonova (48)

In k-space of graphene, the conduction band meets the valence band at the Fermi points, the points of the zero band gap, see Fig. 1.4 (d). When the graphene sheet is rolled up, if 3 is a factor of $n_1 - n_2$, the points of zero band gap of graphene will be crossed by the allowed k lines, as shown in Fig. 1.4 (e), and give a small band gap device. The gap is of the order $\sim < 100$ meV, separating the conduction band and valence band, which is due to perturbations like curvature, twist, or local strain on an originally metallic nanotube.

If 3 is not a factor of $n - m$, the points of zero band gap of graphene will be missed by the allowed k lines, as shown in Fig. 1.4 (f), and give a big band gap device. The resulted conduction and valence bands of the electron state close to the Fermi points of the SWNT, the rolled up sheet of graphene, is shown in Fig. 1.4 (g). The gap is about $0.7 \text{ eV}/D[\text{nm}]$, where $D[\text{nm}]$ is the diameter of the tube in nanometers.

For the special case $n = m$, called an armchair carbon nanotube, the device is metallic and the gap is zero, shown in Fig. 1.4 (b).

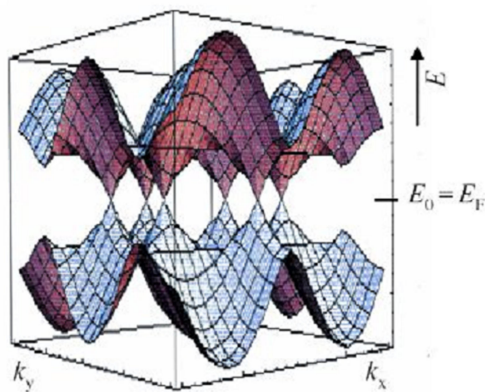


Figure 1.4 (d) – The dispersion relation of graphene, adopted from Minot – The energy of valence and conductance states in graphene is plotted as a function of wave-vector $\mathbf{k}$. The valence and conductance states meet at singular points in k -space called K points. Dispersion around these points is conical. (47)

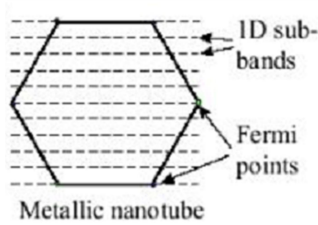


Figure 1.4 (e) – Imposing the boundary conditions of the band structure leads to allowed states on the equidistant lines in k -space, adopted from Sazonova – For a metallic or small gap SWNT, the lines cross the points of zero band gap (the Fermi points). (48)

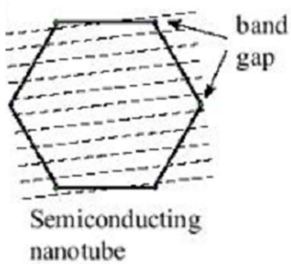


Figure 1.4 (f) - Imposing the boundary conditions of the band structure leads to allowed states on the equidistant lines in k -space, adopted from Sazonova – For a big gap SWNT, the lines miss the points of zero band gap (the Fermi points). (48)

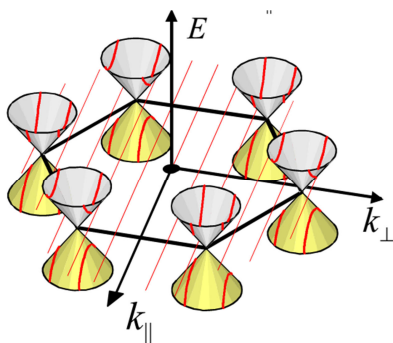


Figure 1.4 (g) – Quantization of wave states around a graphene cylinder, adopted from Minot – Electron states near E_F are defined by the intersection of allowed $\mathbf{k}$ with the dispersion cones at the K points. (47)

Field-Effect Transistor

An electrostatic field can place the Fermi energy of the carbon nanotube in the valence band, the band gap, or the conduction band. This will modify the conductance of the nanotube.

Fig. 1.5 (a) shows the conductance of one of our devices (YB14) as a function of an applied constant electric field between the nanotube and an electrode (gate) about $500\text{ }\mu\text{m}$ away ($V_{\text{gate}} \equiv V_g$) when the gate voltage is lower than 0.35 V , the Fermi surface is in the valence band, as Fig. 1.5 (b), so the transport through the carbon nanotube is due to holes. When the gate voltage is about 0.35 V to 0.5 V , the Fermi energy is in the band gap, as Fig. 1.5 (c), and the transport is off. When the gate voltage is higher than about 0.5 V , the Fermi energy is in the conduction band, as Fig. 1.5 (d), so the transport through the carbon nanotube is due to electrons.

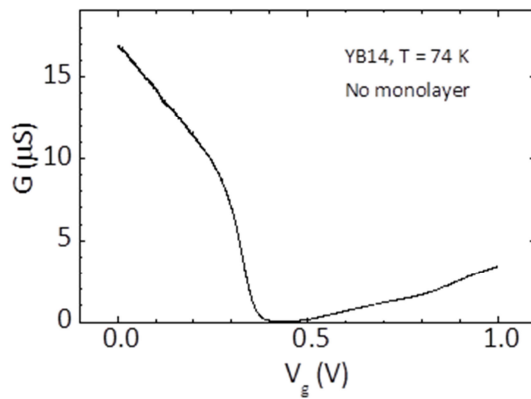


Figure 1.5 (a) – Conductance versus gate voltage of YB14, at $T = 74\text{ K}$, with no adsorbates monolayer

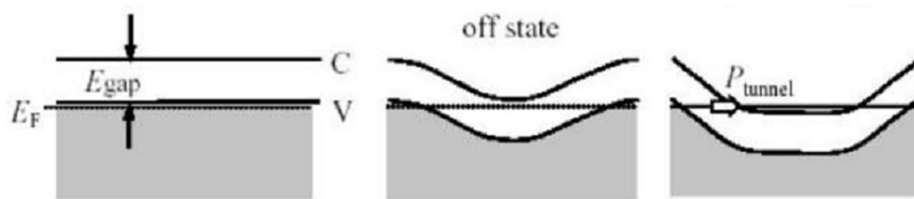


Figure 1.5 (b) – Band diagram of carbon nanotube field effect transistor (FET), adopted from Sazonova – Fermi level passes the valence band, showing “p” regime of operation. (48)

Figure 1.5 (c) - Band diagram of carbon nanotube field effect transistor (FET), adopted from Sazonova – Fermi level is in the gap for a big range, showing “off” regime of operation. (48)

Figure 1.5 (d) - Band diagram of carbon nanotube field effect transistor (FET), adopted from Sazonova – Fermi level tunnels through the gap, passes the conductance band, and tunnels through the gap again, showing “n” regime of operation. (48)

Generally speaking, carbon nanotubes are rigid (stiffest material known), inert, small, nano-meter diameter cylinders (between 1 and 3 nm in diameter and 500 to 1500µm long). They have low mass density, and large Young’s modulus is about 20 GPa $\sim$ 1 TPa (49), such that they make good NEM resonators, sensitive mass sensors (50) (48) (51) (52) (53) (54). With high carrier mobilities, they can make high performance nano-electronics devices. The long and thin shape of the SWNTs makes them ideal for one-dimensional (1D) physics study. They can be either 1D metals or semiconductors, and have clean 1D electronic transport characteristics (55) (56). The coupling between mechanical vibration and electron transport may be strong (57).

Metal carbon nanotubes have good conductance and the conductance of semi-conducting carbon nanotubes strongly depends on electric fields applied to it. Semi-conducting carbon nanotubes can be switched between insulating or conducting by an outside electric field. So the carbon nanotubes are good field effect transistors, and of interest for nano-electronics applications, for example, nonvolatile memory elements, and charge sensors. Because of the small size and mass, they are also ideal for studying quantum size effects. The SWNTs make a clean, homogeneous substrate for physisorption, maybe defect-free.

1.4 Previous Work

In 1991 multi-walled carbon nanotubes (MWNTs), nanotubes with two or more concentric shells, were observed by Iijima in transmission electron microscope images. In 1993, Iijima and Bethune discovered single-walled carbon nanotubes (SWNTs), nanotubes with only one shell.

Since being discovered, carbon nanotubes (CNTs) have been in great interests. Adsorption on carbon nanotube bundles or individual nanotubes was measured. People studied the coverage of adsorbates on nanotubes, binding energy and isosteric heat of the gases on nanotubes, and effects of adsorption on properties of carbon nanotubes (58) (59) (60).

I use mechanical vibration resonance and electrical conductance to study individual, suspended single-walled carbon nanotubes. So, in this section, I will give a brief introduction to some previous work about the vibration of CNTs and the effects of adsorption on conductance of CNTs.

Study of the vibration resonance of carbon nanotubes

Multi-walled carbon nanotubes were used as resonators to measure their elastic modulus. A fiber composed of MWNTs (61) and individual MWNTs (62) were grown on a holder and were placed in situ in a transmission electron microscope (TEM) and in an oscillation electric field which was created by an AC voltage, while a DC voltage was applied to control the charging on the carbon nanotube, as Fig. 1.6 (a), 1.6 (b), and 1.6 (c). The vibration amplitude had a peak when the AC field frequency matched the nanotube resonance frequency, as Fig. 1.6 (d). They obtained the resonance frequency by changing the

frequency of the AC field and observing the vibration of the nanotubes in the TEMs. They compared the bent carbon nanotube with a cantilevered elastic beam, and expected the resonance frequency of the nanotubes' deflection to satisfy the following equation from the Bernoulli-Euler analysis of cantilevered beams.

$$v_j = \frac{\beta_j^2}{8\pi} \frac{1}{L^2} \sqrt{(D^2 + D_i^2)} \sqrt{\frac{E_b}{\rho}}$$

where D is the outer diameter of the investigated nanotube, D_i is the inner diameter, and L is the length, E_b is the elastic modulus, ρ is the density, β_j is a constant for the j -th harmonic. The bending modulus of the multi-walled nanotubes produced by arc discharge (61) is about 10 times larger than the multi-walled carbon nanotubes produced by pyrolysis (62).

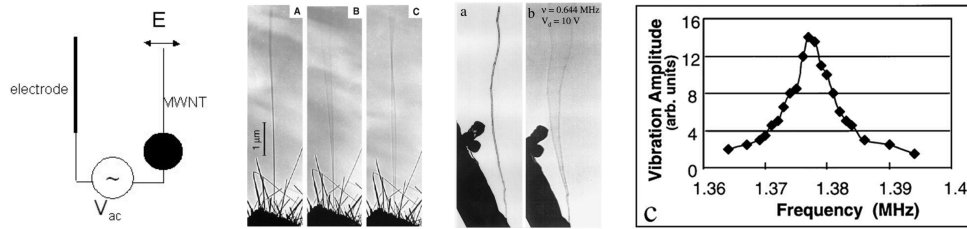


Figure 1.6 (a) – Experimental schematic for experiments of CNT resonators by Poncharal and Gao – The figure is adopted from Sazonova (48)

Figure 1.6 (b) – Nanotube response to resonant alternating applied potentials of Poncharal's experiments, adopted from Poncharal (61)

Figure 1.6 (c) – A carbon nanotube at the stationary and the first resonance mode of Gao's experiments, adopted from Gao (62)

Figure 1.6 (d) – The vibration amplitude versus oscillating voltage frequency of the resonance peak measured from another nanotube, adopted from Gao (62)

In 2002, Purcell et al. (63) grew multi-walled nanotubes by chemical vapor deposition (CVD). Being grown by CVD, the carbon nanotubes are normally defect-free. The carbon nanotube was grown on the end of a Ni tip, and placed between two electrodes, as Fig 1.7 (a). An ac electric field due to an ac voltage applied to the electrodes was used to actuate the nanotube. A dc electric field was created by a dc voltage applied to the holder. This dc field induced the charging on the nanotube, and applied a dc electric force on it. They used the field emission (FE) current, $I_{FE}(v)$, that is emitted from the MWNT, to observe the response as a function of frequency. The FE patterns specific to individual MWNTs are distinguishable. When the MWNT was in resonance, the average electric field at the apex of the MWNT varied so that $I_{FE}(v)$ varied, as Fig. 1.7 (b). The resonance frequency was expected to follow the following equations.

$$\nu_R(V_A) \approx \nu_{R0} + pV_A; \nu_{R0} = \frac{n}{L^2} \sqrt{\frac{EI}{\rho_L}}; p = \frac{n\gamma}{2L} \sqrt{\frac{1}{\rho_L}}; \gamma \equiv r_e \beta_0 V_A \sqrt{\pi \epsilon_0 / 2}$$

where ν_R was the natural mechanical resonance of the nanotube, V_A was the direct voltage applied to the Ni tip, E was the Young's modulus, $I \cong (\pi/4)r^4$ was the cross sectional area moment of inertia with r being the radius of the MWNTs, L was the length of the MWNTs, ρ_L was the mass per unit length, n was the offset depends only on the mechanical properties of the tube, r_e was an effective radius of the emission zone, β_0 was the maximum value of β , the field amplification factor, in the emission zone.

The observed resonance frequencies, ν_R , as a function of the direct voltage, V_A , were straight lines, as Fig. 1.7 (c), consistent with the expectation.

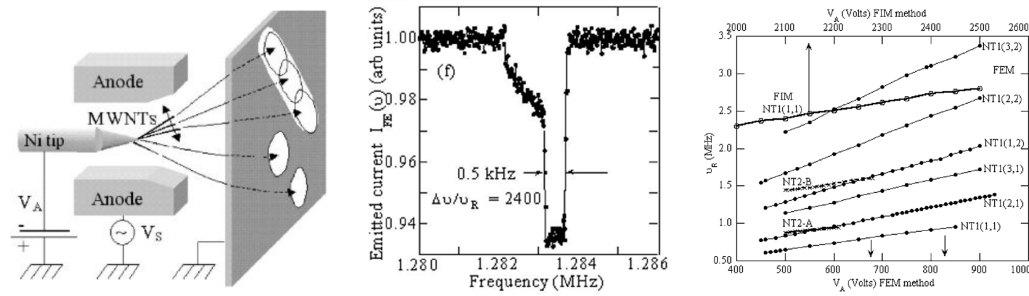


Figure 1.7 (a) – Schema of the experimental field emission setup used to measure the resonances (distances: tip anode ~ 2 mm, tip screen ~ 3 cm, and screen size ~ 4 cm), adopted from Purcell (63)

Figure 1.7 (b) – Total FE current $I_{FE}(\nu)$ as a nanotube, NT1, was scanned through resonance, adopted from Purcell (63)

Figure 1.7 (c) – Dependence of a selection of ν_R 's on V_A for nanotubes, NT1 and NT2, adopted from Purcell (63)

V. Sazonova et al (2006) demonstrated the first tunable self-detecting carbon nanotube resonator, and investigated the tunability of the resonance frequency. They developed a fabrication procedure for suspended carbon nanotubes with a transistor geometry, excited and detected the carbon nanotube vibration modes electrically, described the results, and discussed the limits of the resonance measurements. (50) (48)

They prepared devices by two different procedures. For one procedure, first they grew the carbon nanotubes with the chemical vapor deposition method, after that, they made electrical contacts on top of the two ends of a nanotube by evaporation, and finally etched the SiO_2 of the wafer to suspend the nanotube. The results of the wafer with the nanotube are shown in Fig. 1.8 (a)(b). For the other procedure, they made the electrical contacts first, then etched the SiO_2 of the wafer, and finally grew the carbon nanotubes on top of the electrical contacts. The result is shown in Fig. 1.8 (c). With the

second procedure, the carbon nanotubes would be cleaner since they did not touch the evaporation or etching.

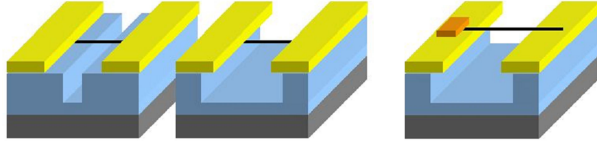


Figure 1.8 (a), (b) – After growth of a CNT, electrodes being defined on top of the catalyst pads, and a wet-etch step followed, adopted from Sazonova (48)

Figure 1.8 (c) – An alternatively way, a CNT being grown last, on top of the deposited Pt contacts over a predefined trench, adopted from Sazonova [Thesis of Sazonova, 2006]

The two ends of a carbon nanotube were fixed on or below two electrical contacts which were going to work as source and drain of current passing through the nanotube. The nanotube was suspended, and under the tube there is a gate shown in Fig. 1.9. The gate voltage V_g , which induced charges $q = C_g V_g$ on the nanotube, had two components, the static (DC) voltage, V_g^{DC} , and the time-varying (AC) voltage, δV_g . C_g was the capacitance between the gate and the tube, and depended on the distance between the nanotube and the gate, z .

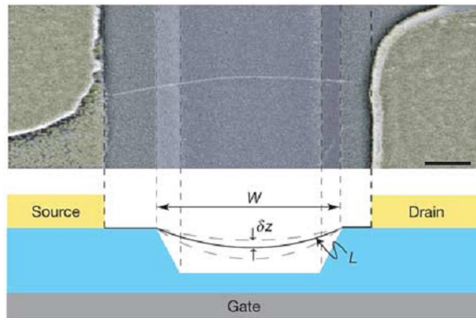


Figure 1.9 – Device geometry schematic, adopted from Sazonova – The false-colored SEM image of a suspended device was taken at a 45° angle. (48)

with applied source-drain voltage bias, δV_{sd} , the current passing through the tube was expected to be

$$\delta I^{lock-in} = \delta G \delta V_{sd} = \frac{1}{2\sqrt{2}} \frac{dG}{dV_g} (\delta V_g + V_g^{DC} \frac{\delta C_g}{C_g}) \delta V_{sd}$$

where δG was the variance of the conductance G , and δC_g was the variance of the capacitance between the gate and the tube, C_g . Since δC_g depended on z , the vibration of the nanotube can be detected in

the passing current. When the vibration frequency matched the resonance frequency of the nanotube, there was a sharp jump in the current.

They set the AC frequency of δV_{sd} to be $\omega + \Delta\omega$, the AC frequency of V_g to be ω , and then tracked the component of the current which had frequency $\Delta\omega$, where ω was often in the range of 3 – 200 MHz, $\Delta\omega$ was set to be 10 kHz. An alternative way was that the gate voltage V_g was fixed to be static, an AM modulated voltage V_{sd}^ω was applied to the source electrode, and the current passing the nanotube was detected at frequency $\Delta\omega$ which was the AM modulation frequency (1 kHz or 400 Hz).

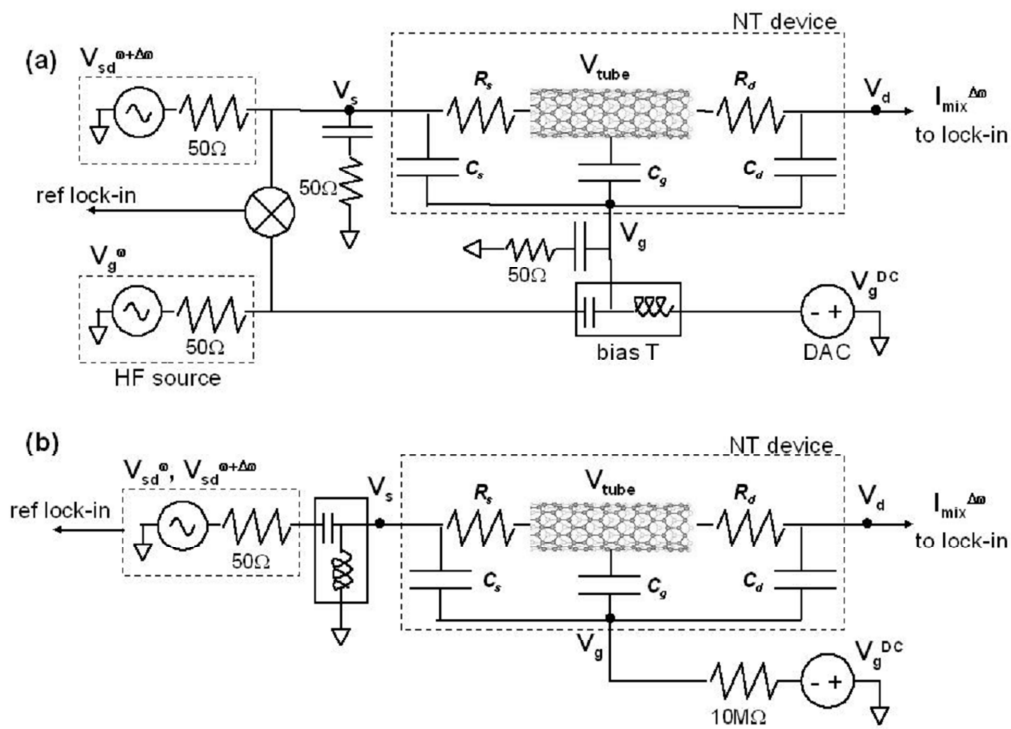


Figure 1.10 (a) Schematic of a two-source circuit setup used to measure resonance frequency of carbon nanotubes, adopted from Sazonova (48)

Figure 1.10 (b) Schematic of a one-source circuit setup used to measure resonance frequency of carbon nanotubes, adopted from Sazonova (48)

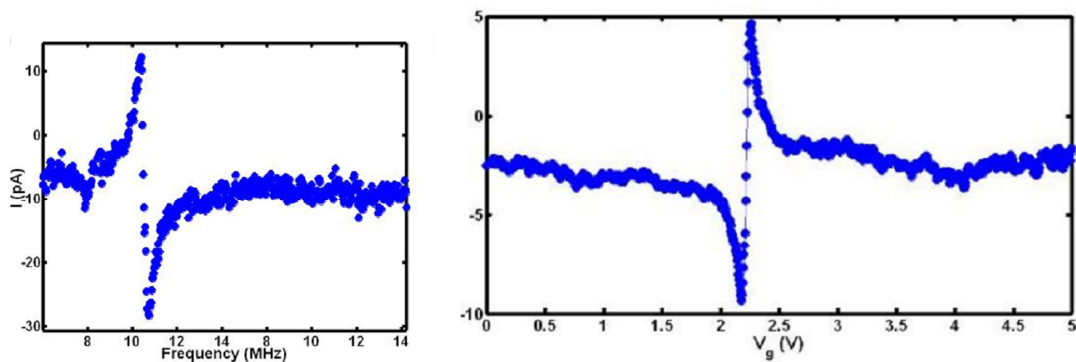


Figure 1.11 (a) - Observed resonance, mixing current as a function of the driving frequency, with gate voltage being fixed, adopted from Sazonova (48)

Figure 1.11 (b) - Observed resonance, mixing current as a function of the gate voltage, with driving frequency being fixed, adopted from Sazonova (48)

Study of adsorption effects on the conductance of devices

In addition to the study of the suspended nanotubes resonance properties, measurements of the electrical conductance of suspended and not suspended nanotubes were pursued. It was found that the electrical properties of carbon nanotubes are sensitive to the adsorption of a gas on its surface and on the electrical contacts to the nanotube.

In 1997, Lee et al. showed that the conductance of single-walled carbon nanotube bundles affected by bromine and potassium adsorbates. (64)

In 2000, Collins et al. used SWNT bundles and thin films of SWNTs to observe the dependence of the resistance of a nanotube exposed to air or O_2 . They mounted the substrates in a vacuum test chamber, measured the resistance with a low bias current, and found that the resistance is very sensitive to the gas exposure with the changing in resistance being reversible (65).

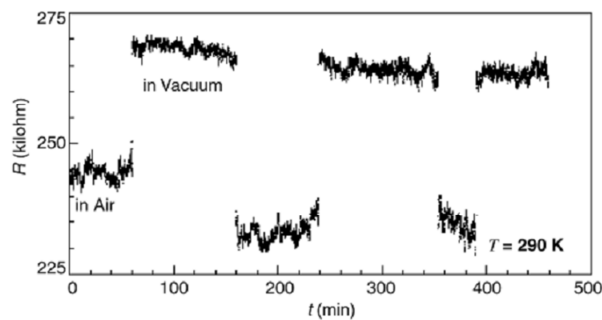


Fig. 1.12 – Reversible change of the resistance of SWNT films to air exposure (65)

Kong et al. studied the sensing of individual semiconducting single-walled carbon nanotubes (S-SWNTs) to toxic gases NO_2 and NH_3 . Exposing the S-SWNTs to NO_2 or NH_3 , they observed the conductance of the tubes increased or decreased. They claimed that S-SWNT sensors can have sensitivity as high as 10^3 at room temperature by biasing the nanotube with a proper electrical gate. (66)

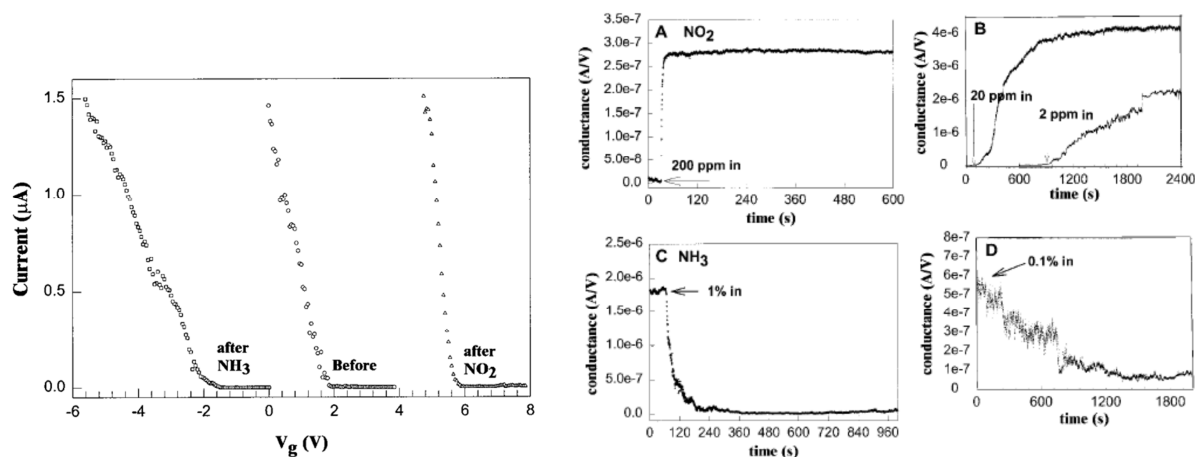


Figure 1.13 – Chemical gating effects to a semiconducting SWNT – The measurements with NH_3 and NO_2 were carried out successively after sample recovery. (66)

Figure 1.14 (a) – Conductance of a semiconducting SWNT versus time, with $V_g = 4$ V, in an initial insulating state, in a 200-ppm NO_2 flow (66)

Figure 1.14 (b) – Data for a different semiconducting SWNT in 20- and 2-ppm NO_2 flow (66)

Figure 1.14 (c) - Conductance of the same semiconducting SWNT in (a) versus time, with $V_g = 0$ V, in an initial conducting state, in a flow of Ar containing 1% NH_3 (66)

Figure 1.14 (d) - Data for a different semiconducting SWNT in 0.1% NH_3 flow (66)

Bockrath et al. reported the effects of potassium adsorption on the conductance on individual semiconducting single-walled carbon nanotube ropes. They found that the adsorbates changed the conductance from zero to a value of $1 \mu\text{S}$, and explained that by the potassium donating electrons to the nanotube rope and resulting in mobile charge carriers at the Fermi level. (67)

Sumanasekera et al. demonstrated that the conductance and thermoelectric-power of nanotube devices can be modified by exposure to N_2 and He. They studied the effects of gas adsorption on conductance of mats of tangled SWNTs. (68)

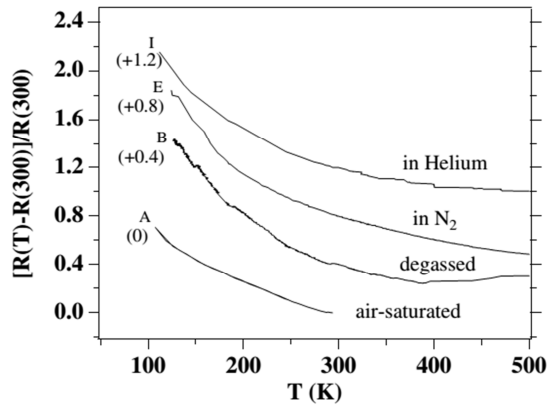


Figure 1.15 – Normalized resistivity, $(R(T)-R(300))/R(300)$, for mats of SWNT bundles versus temperature – N_2 and He were admitted to a pressure of ~ 1 atm at 500 K, sealed the system, and cooled down. The curves had been offset vertically by the amount indicated in parentheses to the left of each curve. Vacuum pumping was applied at A, E, and I, while N_2 was introduced at B. (68)

In the same year, Zhou et al. observed modulated chemical doping on individual single-walled carbon nanotubes (SWNTs). The individual SWNTs were grown on catalytically patterned SiO_2 surface, and were connected by the source and drain metal electrodes. A polymethylmethacrylate (PMMA) layer covered half of a nanotube, and the other half of the nanotube was left exposed to potassium atoms, shown in Fig. 1.16 (a), (b). The half part of the nanotube covered by PMMA remained p-type, while adsorption of potassium atoms changed the other half part of the nanotube from p-type to n-type, shown in Fig. 1.16 (c). Current versus back-gate voltage (I - V_g) was measured, shown in Fig. 1.17 (a), (b), (c). They also claimed that, along a nanotube, controlled doping modulations over a length scale <100 nm would lead to well-defined quantum systems. (69)

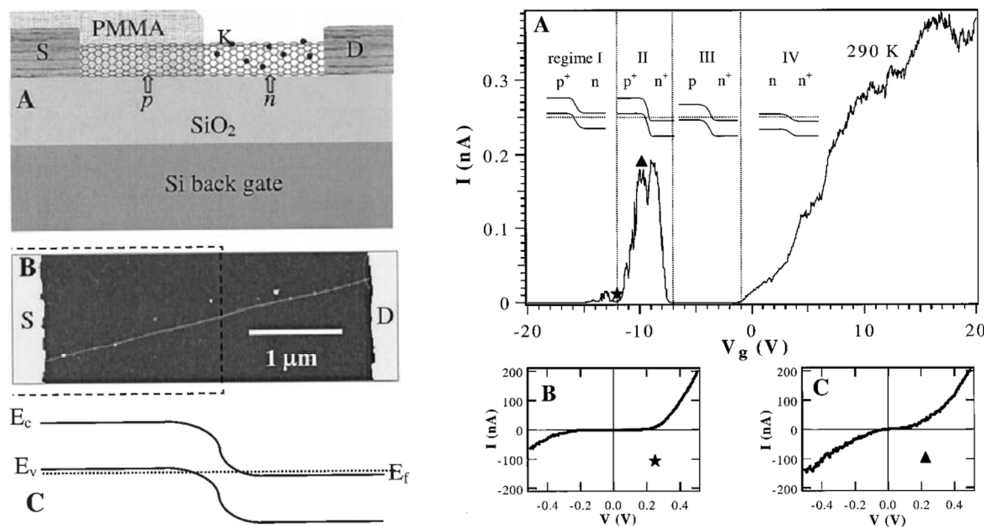


Figure 1.16 (a) – An SWNT with modulated chemical doping – The SWNT was contacted by two Au electrodes. The right half of the SWNT was in the exposure of K atoms (black dots), while the left half was covered by PMMA. (69)

Figure 1.16 (b) – Atomic force microscopy image of the SWNT before PMMA coating and K atoms doping (69)

Figure 1.16 (c) – A band diagram for the system after PMMA coating on the left half of the SWNT and K atoms doping on the right half – E_c , E_f , and E_v represent the conduction band, Fermi level, and valence band, respectively. (69)

Figure 1.17 (a) – Current of the modulation-doped SWNT versus gate voltage, I - V_g , recorded under a bias voltage $V = 1$ mV, at room temperature (69)

Figure 1.17 (b) – Current versus bias voltage curve recorded in the regime I in Fig. 1.17 (a) (69)

Figure 1.17 (c) - Current versus bias voltage curve recorded in the regime II in Fig. 1.17 (a) (69)

In 2002 Single-walls carbon nanotubes were found to be able to be doped by O₂ and K by Derycke et al.. They used single-walled carbon nanotubes dispersed on gold electrodes which were pre-patterned on an oxidized silicon wafer, and claimed that the main effect of oxygen adsorption was not to dope the bulk of the nanotube, but was to modify the barriers at the metal-semiconductor contacts. (70)

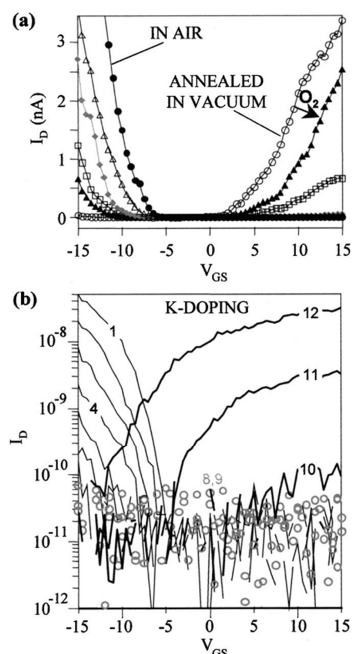


Figure 1.18 (a) – Effect of O₂ impurities on the conductance of an n-FET SWNT produced by thermal annealing (open circles). The O₂ exposures are: 2minute at $P = 10^{-4}$ Torr (black triangles), $P = 5 \times 10^{-4}$

Torr (open squares), $P = 5 \times 10^{-3}$ Torr (gray diamonds), $P = 10^{-1}$ Torr (open triangles) and exposure to the ambient (black circles) (70)

Figure 1.18 (b) – Effects of K atom doping on a CNTFET – The FET is initially p-type. After seven doping cycles (curves 1-7), no more current can be detected (open circles 8, 9). At higher doping levels, the device becomes n-type (curves 10-12). (70)

Sumanasekera et al. observed the effect of cyclic hydrocarbons C_6H_{2n} ($n = 3-6$) adsorption on resistance and thermoelectric power of single-walled carbon nanotube films. (71)

In 2003 Someya et al. studied the effect of alcohol on nanotube transistors, see Fig. 1.19, 1.20, 1.21. They synthesized SWNTs by CVD, fabricated field-effect transistor (FET) structures, and measured the drain current while the SWNTs were exposed to alcoholic vapors, see Fig. 1.20 (a), (b). When saturated ethanol vapor was delivered to the sensor surface, first a significant change happened in the drain current (for some cases, there was a sharp spike at the start of the change), and then the current gradually reached a stable value, see Fig. 1.20, Fig. 1.21. (72)

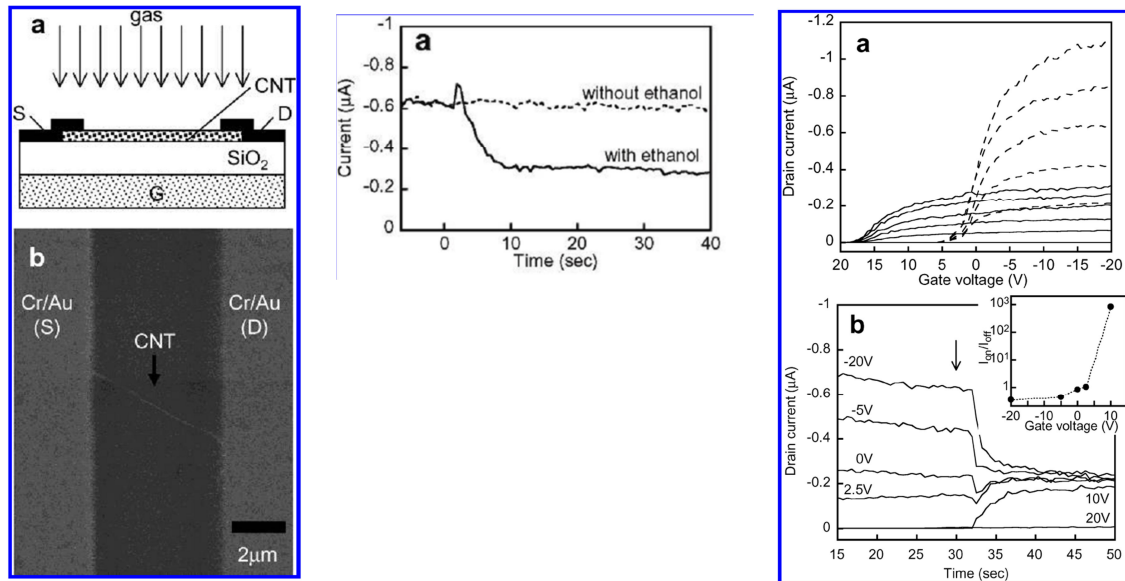


Figure 1.19 (a) – Cross-sectional structure of a nanotube field-effect transistor (FET) - The experimental geometry was schematically shown. (72)

Figure 1.19 (b) – A scanning electron microscopic image of a part of a nanotube FET – The single-walled carbon nanotube bridged source and drain electrodes with spacing of 5 μm. (72)

Figure 1.20 – Drain current measurements as a function of time with a source drain bias of 100 mV and a gate voltage of 10 V (72)

Figure 1.21 (a) – FET characteristics measured with and without application of a saturated vapor of ethanol are shown in the dash line and the solid line, respectively – The six dash and solid lines are for source-drain bias voltage from 0 to -100 mV, in steps of -20 mV. (72)

Figure 1.21 (b) – The responses to a saturated vapor of ethanol were measured with different gate biases – The arrow indicates the time at which alcohol is introduced. The inset shows the ratio of drain current (I_{on}/I_{off}) with and without application of alcohol as a function of gate voltage. (72)

In 2004, Romero et al. studied the effects of physisorption of various alcohol molecules ($C_nH_{2n+1}OH$; $n = 1-4$) on the resistance and thermoelectric power of thin films of bundled single-walled carbon nanotubes. (73)

In 2005, the effect of N_2 on the conductance of a carbon nanotube sheet was measured by Huang et al. They grew the vertically aligned carbon nanotubes, see Fig. 1.22, by using thermal chemical vapor deposition (thermal CVD). With zero gate voltage and source-drain bias being 10 V, they found that exposure to N_2 increased the resistance of the CNTs, see Fig. 1.23, and higher N_2 pressure made the resistance higher. They claimed that applying a high source-drain voltage increased the sensitivity for sensing N_2 . They also demonstrated that applying a negative gate voltage improved the sensitivity. (74)

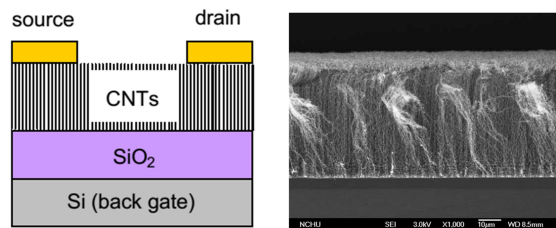


Figure 1.22 (a) – Schematic cross section of the three-terminal gas sensor with the silicon substrate as back gate (74)

Figure 1.22 (b) – Typical cross-sectional SEM images of the vertical aligned CNTs mat (74)

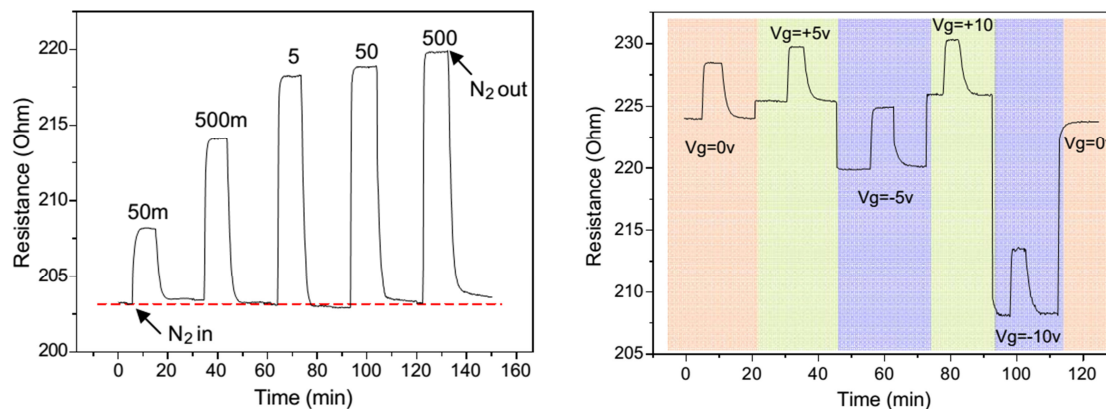


Figure 1.23 (a) – The electrical resistance between source and drain at 10 V bias voltage without any gate voltage under various N₂ filling pressure from 50 mTorr to 500 Torr (74)

Figure 1.23 (b) – The electrical resistance of CNTs mat measured at a fixed 5 V source drain bias voltage while applying various gate voltages under a 5 Torr N₂ pumping and filling environment (74)

Romero et al. (75) studied the electron transport in metallic single-walled carbon nanotubes under collisions with inert gas atoms or small molecules. By using thin films of bundled nanotubes, they observed the sensitivity of resistance of the thin film of metallic CNTs to He, Ar, Ne, Kr, Xe, CH₄, and N₂. They claimed that the transient deformation in the wall of the nanotube might provide scattering mechanism which might be used to explain the atom collision-induced changes in nanotube electrical transport.

In 2005, Liu et al. separated the effects adsorbates have on the nanotubes and on the tube-electrode contact by measurements with NH₃ and NO₂. They fabricated CNT-FET devices by using chemical vapor deposition (CVD), and grew SWNTs on silicon substrates with the thermal oxide gate dielectric layer. They exposed the contacts, see Fig. 1.24 (a), and the center part, see Fig. 1.24 (b), of the nanotube devices to NO₂, NH₃, or air. They observed that, no matter whether the devices are contact-exposed or center-exposed, NO₂ shifts the threshold voltage positively and NH₃ shifts the voltage negatively, see Fig. 1.25. (76)

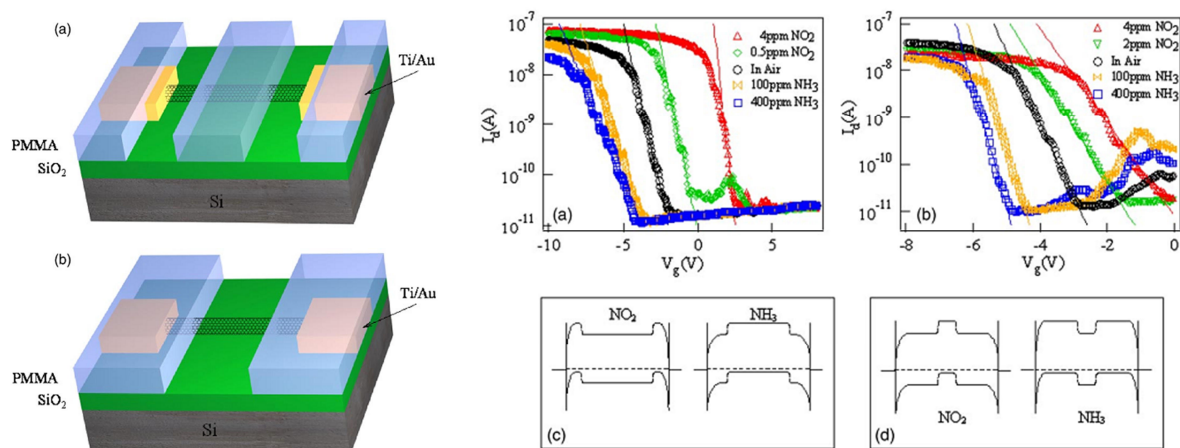


Figure 1.24 (a) – Schematics of a contact exposed CNT transistor (76)

Figure 1.24 (b) - Schematics of a center exposed CNT transistor (76)

Figure 1.25 (a) – I_d versus V_g of a contact exposed device under various ambient conditions (76)

Figure 1.25 (b) – I_d versus V_g of a center exposed device under various ambient conditions (76)

Figure 1.25 (c) – The band structure of the contact-exposed device in NO₂ and NH₃ at the threshold voltage (76)

Figure 1.25 (d) - The band structure of the center-exposed device in NO₂ and NH₃ at the threshold voltage (76)

Adrian Bachtold's group [] also studied the effect of adsorption on a suspended nanotube. They already had data several years ago.

Adsorbates on carbon nanotubes do not only affect the conductance and the thermoelectric power (77) (71). Some other properties of single-walled carbon nanotubes, for example capacitance, are also highly sensitive to a broad class of chemical vapors (78), but we are not going to discuss it here.

The work of Z. Wang et al. in University of Washington

In 2010, Z. Wang et al. published resonance measurements for adsorption on suspended, grown in-situ, single-walled carbon nanotubes, simultaneously measuring the equilibrium pressure of the adsorbate at the temperature of the experiment. (79) (80)

Wang used two generations of devices. For the first generation ones, the fabrication process started with a Si wafer coated with a layer of SiO₂ and a thin layer of Si₃N₄ on top of the SiO₂ layer. He used electron-beam lithography (EBL) to define the windows for trench, electrodes, and catalyst spots, with respect to the processing orders on the wafer, and then performed chemical vapor deposition (CVD) to grow the carbon nanotubes. At the step of etching the SiO₂ by buffered oxide etch (BOE) for trenches, it was found that if the Si₃N₄ layer is a low-pressure chemical vapor deposition (LPCVD) one, the etching would be fine, but if it was a plasma-enhanced chemical vapor deposition (PECVD) one, this step might fail. After the CVD growth, SWNTs passing but not touching a trench, and connecting two electrodes at two sides of the trench would be grown, see Fig. 1.26. The process was entirely completed in University of Washington (UW).

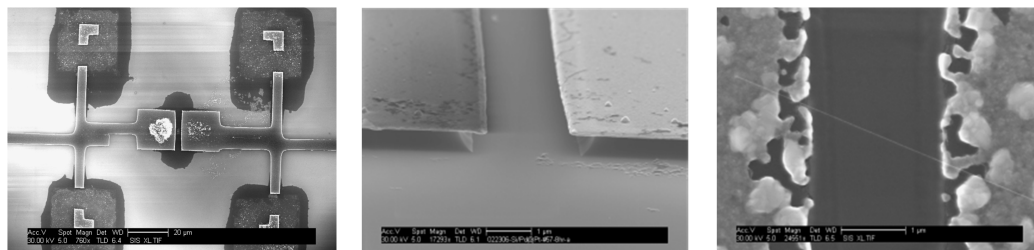


Figure 1.26 (a), (b), (c) – SEM images of a device fabricated at the University of Washington for the whole process – (a) A device is shown. (b) – The trench area is shown. (c) A device is shown. (80)

For the second generation devices, the wafer structure, including trenches and electrodes, was fabricated at the UCSB Nanofabrication Facility. The LPCVD nitride layer was used. The design of the layout was first used by Bockrath group. The CVD growth was done in UW.

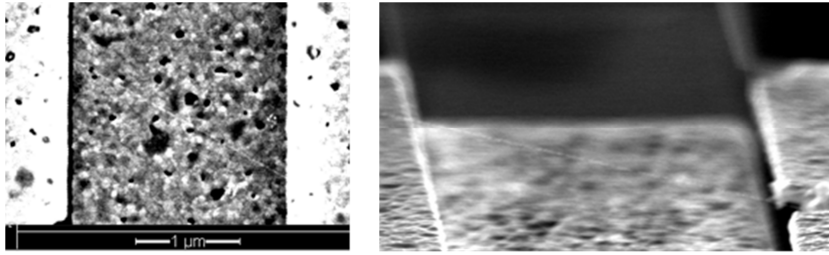


Figure 1.26 (d), (e) – A SEM image of a device made on a wafer with the structure fabricated at UCSB (80)

Wang measured the conductance versus gate voltage ($G-V_g$) of the nanotubes at room temperature first, and then chose quiet, well-connected, small gap ones to study resonances in the mixing current, using V. Sazonova's technique. (50) (48)

Given an amplitude modulated (AM) radio frequency (RF) signal $V_0(1 + m \times \cos(\delta\omega t)) \times \cos(\omega t)$, the mixing current was studied, where V_0 , about 10 mV, was the signal amplitude, m was the modulation strength, and $\delta\omega$ was much smaller than ω , which would be swept through the possible resonance frequency range. A DC voltage was applied to the gate to control the charging, band structure, and Fermi level of the nanotubes, see Fig. 1.27.

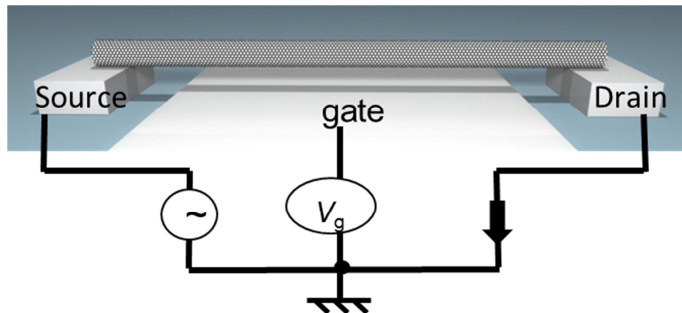


Figure 1.27 (a) – Schematic of the setup - The one source version of Sazonova's setup was chosen. (80)

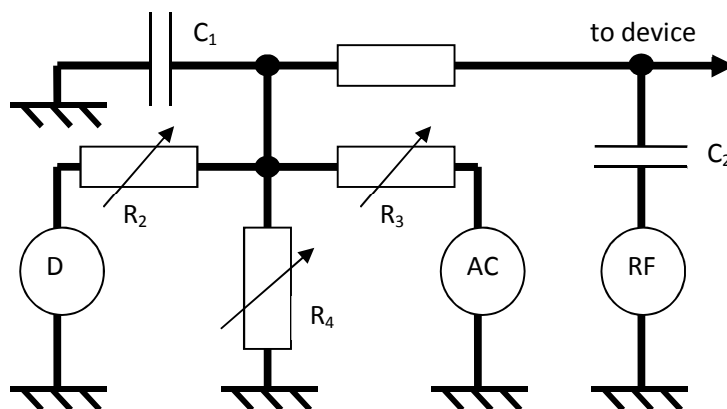


Figure 1.27 (b) – Schematic of the circuit setup – DC: the DC signal. AC: the low frequency AC signal. RF: the AM RF signal. $R_2 = R_3 = 100 \text{ K}\Omega$, and $R_4 = 1 \text{ K}\Omega$, forming two 100:1 voltage dividers. $R_1 = 10 \text{ K}\Omega$, small compared with the resistance of a typical SWNT. Resistance of a typical SWNT was much higher than R_4 . (80)

Wang et al. assumed that the adsorbates were uniform on the nanotubes, so that the resonance frequency, f_{res} , was proportional to $\rho^{-1/2}$, where ρ was the mass density per unit length of the nanotubes, they expected that the coverage ϕ , defined as $\phi \equiv \frac{\text{number of adsorbed atoms}}{\text{number of carbon atoms}}$, satisfied the following equation.

$$\phi \equiv \frac{\text{number of adsorbed atoms}}{\text{number of carbon atoms}} = \frac{m_c}{m_{ads}} \times \left(\left(\frac{f_0}{f_{res}} \right)^2 - 1 \right)$$

where m_c was the mass of a carbon atom, m_{ads} was the mass of an adsorbed atom, f_0 was the resonance frequency with the nanotube being in vacuum, and f_{res} was the resonance frequency with adsorbates being on the nanotube. Fixing the temperature and gate voltage, increasing the gas pressure which the SWNTs were exposed to, they obtained their adsorption isotherms.

Besides the adsorption isotherms, they also measured the conductance of the devices versus gas pressure at a fixed temperature and a fixed gate voltage, and observed conductance isotherms of the devices.

By tracking the single-walled carbon nanotube resonance frequencies, they studied the phase behavior of adsorbed argon and krypton. They observed the formation of monolayers on the SWNT cylindrical surface, phase transitions of the adsorbates, and simultaneous effects on the conductance of the nanotube. It was remarkable that adsorption could be measured on ONE nanotube. Their published results are shown in Fig. 1.28. Some data will be reviewed in the context with my own measurements in Chapter 3 and discussed in Chapter 4.

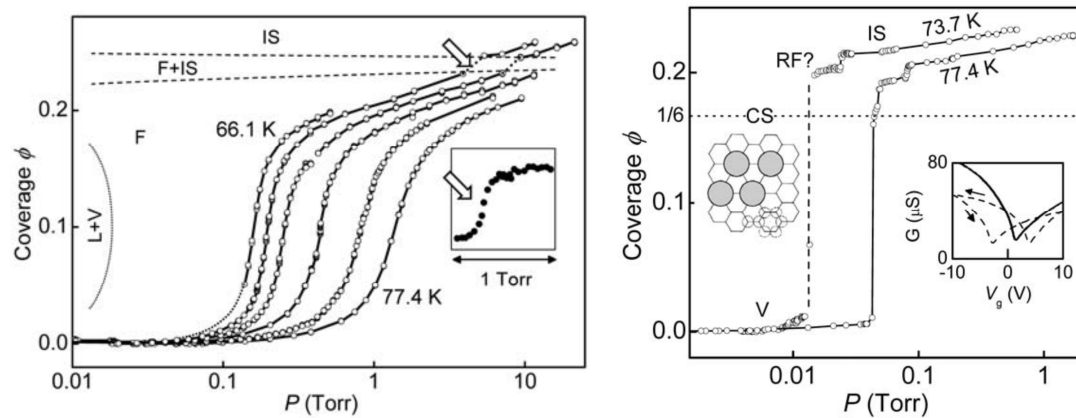


Figure 1.28 (a) – Isotherms of coverage parameter ϕ for Ar on device YB3 – The temperatures are 66.1, 67.7, 68.8, 71.9, 73.9, and 77.4 K. The large step occurred within the super-critical fluid (F), while the smaller step, a separate measurement of which is shown in the inset, occurred at the transition to incommensurate solid state. (79)

Figure 1.28 (b) – Adsorption of Kr on device YB3, showing phase transitions – The dotted horizontal line, $\phi = 1/6$, corresponds to the commensurate solid state of the adsorbed Kr. The left inset shows the commensurate arrangement of adsorbates sitting on carbon hexagons. The right inset shows conductance of YB3 versus gate voltage at room temperature, where the solid line represents the device in vacuum, and the dashed line represents the device in air. (79)

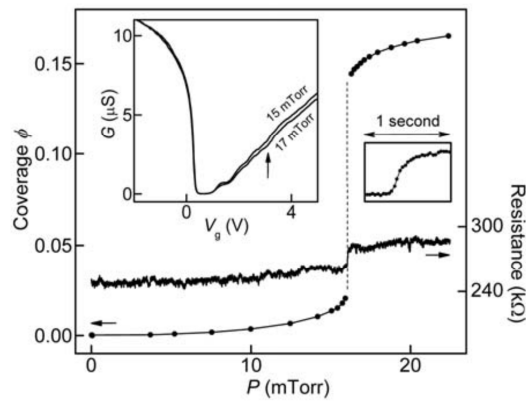


Figure 1.28 (c) – Adsorption and resistance of SWNT YB8 as a function of the pressure of Kr exposure, with the gate voltage being 3.1 V, at $T = 77$ K – The left inset shows conductance of YB8 versus the gate voltage at pressures just below and above the transition, where the arrow indicates the gate voltage 3.1 V. The right inset shows resistance versus time during pressure increasing across the transition. (79)

Chapter 2. Experimental Procedures

In this chapter, I describe the technique we used to fabricate the devices, the equipment setups for the experiments, the data we measure, the data acquisition methods, and the procedure we follow.

2.1 Devices Fabrication

The technique I used to grow my single-walled carbon nanotube devices was adapted from Dai's group at Stanford, see Cao et.al. (2005). (81)

Wafer Preparation

Z. Wang's work in UW is followed. The devices I have used start with an oxidized Si wafer where micrometer size trenches were already etched and Pt electrodes were deposited at the UCSB Nanofabrication Facility. The Pt pads at the edge of the trench will become the source and drain of the future device, and the Pt deposited at the bottom of the trench will become the gate electrode. But, here I use two different designs of the layout of the wafers. One is what Z. Wang got from UCSB before, and was first used by the Bockrath group, see Fig 2.1 (a) below. For wafers with the other design, the electrodes are also patterned at the UCSB Nanofabrication Facility, but the mask is from USC users in Prof. Steve Cronin's group as Fig 2.1 (b).

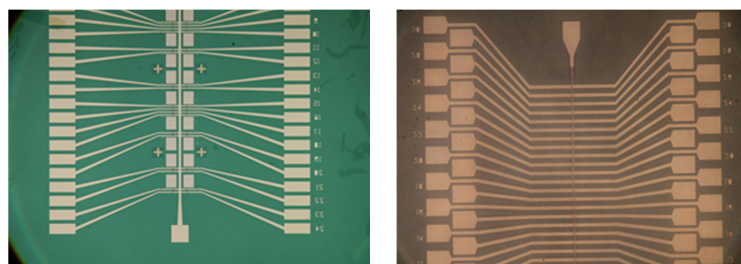


Figure 2.1 (a) – A wafer structured with Pt electrodes deposited at the UCSB Nanofabrication Facility - The design of the layout of the wafer was first used by the Bockrath group.

Figure 2.1 (b) – A wafer structured with Pt electrodes deposited at the UCSB Nanofabrication Facility - The mask is from USC users in Prof. Steve Cronin's group.

For the design of Bockrath group, there is a local gate with respect to every two or four drain electrodes, but all the devices are connected to only one common source. After getting the patterned wafers, we cover the wafer with resist by ourselves, and open windows on the resist to define the positions of the catalyst spots on the wafer.

We drop two drops of 6% PMMA as the resist on a piece of patterned silicon wafer, and spin the wafer to make the PMMA being uniform on it. After baking for 1.5 minutes at 180°C, we use electron beam lithography (EBL) to open windows on the PMMA mask at the Pt source and drain electrodes. The wafer is put in PMMA developer for 70 seconds, and then the wafer is washed with IPA, dried, and baked at 70°C for more than 2 hours.

The catalyst consists of 1 mg MoO_2 , 25 mg FeNO_3 , 15 mg Al_2O_3 , and 15 ml methanol. They are mixed and sonicated for more than one hour. Three drops of the catalyst are put on each wafer. After the wafer is dried naturally, we bake it at 170°C for 3 minutes. We then sonicate the wafer in acetone until the PMMA is gone. The catalyst will be left at the positions of the windows defined by EBL, see Fig. 2.1 (c), (d), (e).

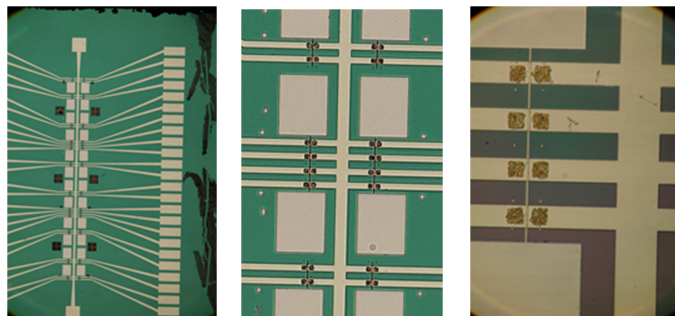


Figure 2.1 (c) – A Pt electrodes deposited wafer with catalyst on designed windows - The layout of the wafer was first used by the Bockrath group.

Figure 2.1 (d) – Enlarge part of Figure 2.1 (c) – The big white squares are local gates, and the much smaller, brown squares are the catalyst spots. We can see how the catalyst spots correspond to the local gates in the figure.

Figure 2.1 (e) – Enlarge part of Figure 2.1 (d) – We can see the catalyst spots clear here.

For the design from Cronin's group, there is a source electrode with respect to each drain electrode, but there is only a common gate. Wafers with this design already have resist on it and catalyst windows are already patterned in the resist when they are sent from UCSB.

We make the catalyst with MoO_2 , FeNO_3 , Al_2O_3 , and water since the resist used on these wafers can be dissolved by methanol. About two drops of the catalyst are put on each wafer. The wafer is dried when we bake it. (The catalyst with water being the solution takes a long time to be dried naturally.) Different temperatures and time are tried to get good results. We then wash the wafer with acetone, or sonicate the wafer in acetone until the PMMA is gone. The catalyst will be left at the positions of the windows of the resist patterned, see Fig. 2.1 (f), (g).

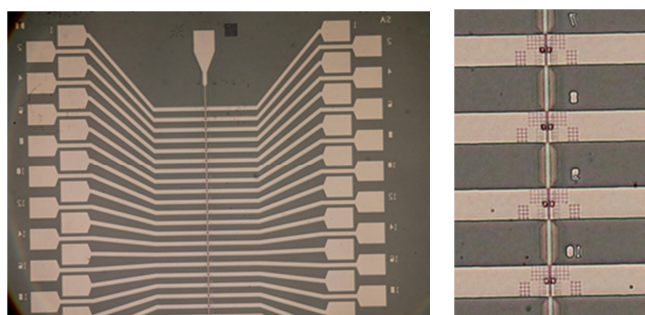


Figure 2.1 (f) – A Pt electrodes deposited wafer with catalyst on designed windows - The mask is from USC users in Prof. Steve Cronin's group.

Figure 2.1 (g) – Enlarge part of figure 2.1 (f) – The small brown squares are the catalyst spots.

Chemical Vapor Deposition (CVD)

We put the wafer into a tube furnace and let H_2 flow through the tube with a flow rate 400 ml/min for 8 minutes at room temperature. The tube furnace is then heated up to 800°C , with 400 ml/min H_2 passing the tube through the heating process. After the temperature arriving at 800°C , we increase the H_2 flow rate to 600 ml/min, and add CH_4 flowing with a flow rate 325 ml/min besides the H_2 flow for 5 minutes. Then, we close the CH_4 flow, but let the 600 ml/min of H_2 flow continue passing for 2 more minutes, and then we cool down the oven. After the temperature is lower than 700°C , the flow rate of H_2 is decreased to 100 ml/min. When the temperature is down to $100\sim 200^\circ\text{C}$ we take out the wafer with the carbon nanotube devices, and put it into a vacuum chamber. Fig. 2.2 below shows an electron microscope image with a suspended nanotube grown as described.

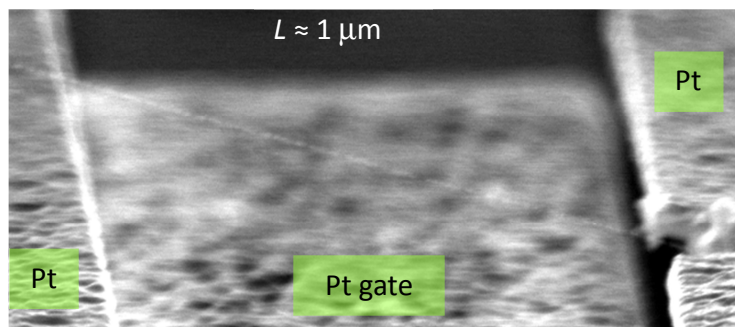


Figure 2.2 - A SEM image of a single-walled carbon nanotube from our previous work

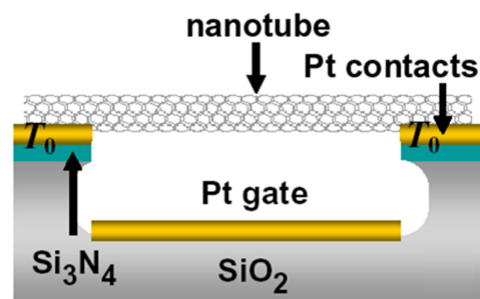


Figure 2.3 - A cartoon which shows the structure of the nanotube, source, drain and gate, not in scale - In the real devices, the length of the nanotube is longer than 500 times of its diameter. Technique - Dai group (Stanford) (81)

Device Assembly

The next step is to probe the Si wafer to find out whether a suitable carbon nanotube has grown between the pads, and whether no short circuits exist. We use an optical microscope and probes to check the current-gate voltage characteristic and the level of noise in the device. If a suitable device or devices are found, we glue the wafer onto a standard 14 pin socket, and use gold wire to bond the electrodes on the wafer to the electrodes on the socket. The socket is mounted into a cell, as Fig. 2.4 (a), of about 100 cc volume. Jumping wires are used to connect the electrodes to the voltage sources so current can pass from the source through the nanotube and come back from the drain, and the gate voltage can be varied.

2.2 Experimental set-up

The cell is closed with an Indium o-ring as shown in Fig. 2.4 (b). The cell is mounted on a cryocooler with a temperature range of 4.3 to 350K, as Fig. 2.4 (c). It is connected to a gas dosing system via a gas tube. The gas dosing system has three capacitance gauges having ranges of 0.250, 10 and 1000 Torr. An oil-free turbo molecular pump cart provides the vacuum. Several high purity gas tanks are permanently attached to the system.

The cell is covered by a metal shell connected to the first stage of the cryocooler to minimize room temperature radiation. An outside metal shell, see Fig. 2.4 (c) is the vacuum enclosure. The area between the cell and the outside shell is kept in vacuum during experiments. The experimental temperature is regulated by an electronic controller.

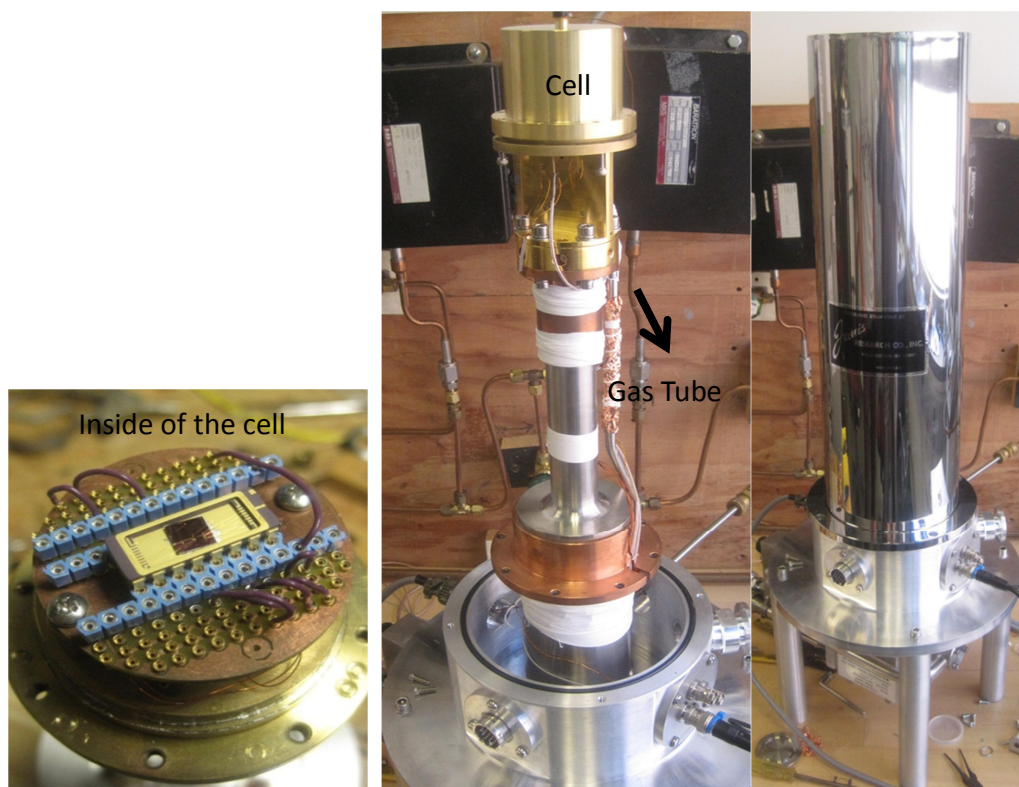


Figure 2.4 (a) – Image of a wafer glued on a socket which was mounted in the cell

Figure 2.4 (b) – Image of the closed cell and a gas tube inside the cryo-cooler

Figure 2.4 (c) – Image of the closed cryo-cooler

For our first setup, the vacuum chamber was submerged in a liquid nitrogen bath whose temperature T could be changed over a small range (68 K to 77.4 K). (Carbon nanotubes YB3 and YB8 were measured with the first setup. Starting with device YB10, the current setup has been used.)

2.3 Resonance frequency measurement

To measure an adsorption isotherm, we setup the temperature for an adsorption isotherm according to the gas being studied. We will add gas from room temperature and measure the equilibrium pressure. The mass adsorption is detected using the resonance technique described in Chapter 1.

We detect a resonance frequency, f_{res} , using the so-called mixing technique [ref 1, 2, 3]. A block diagram of the complete frequency measurement setup is shown in Fig. 2.5. A signal at radio frequency f in the range 10 MHz to 500 MHz, modulated at $\delta f = 1$ kHz, is applied to the source. The resulting current component at δf is detected using a current amplifier and a lock-in detector referenced to δf . At resonance this “mixing current” shows a feature produced by the nonlinearity due to the changing gate capacitance as the nanotube vibrates with an enhanced amplitude, see Fig. 2.6.

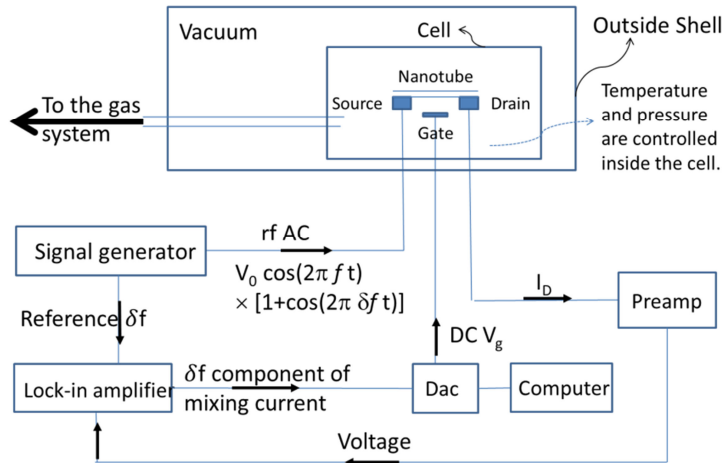


Figure 2.5 - A block diagram of the frequency measurement setup

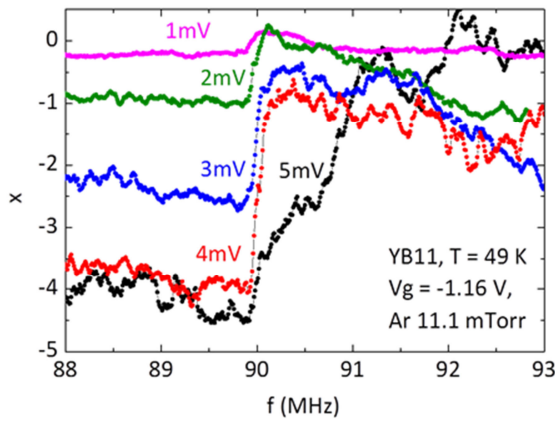


Figure 2.6 - The x component of the mixing current versus frequency of the r.f. signal applied to the source around the resonance region with some different voltage amplitudes applied - The signal-walled carbon nanotube is YB11, and the measurement is done with Ar pressure 11.1 mTorr, at $V_g = -1.16$ V, $T = 49$ K.

V_g is chosen to obtain the clearest possible resonance, the temperature is set, and a narrow sweep of f around f_{res} is done for the bare nanotube and as the pressure in the chamber is incremented in small steps.

Adsorption increases the mass per unit length of the nanotube, which lowers f_{res} .

Adsorption isotherms

The result is an isotherm of f_{res} vs. P at given T . To convert f_{res} to a measure of mass adsorbed (the "coverage"), we assume f_{res} is inversely proportional to the square root of the mass of the nanotube plus adsorbate. This is correct if the adsorbate is uniformly distributed and the vibrations are linear, and it

turns out to work surprisingly well. With this assumption the coverage is given by

$$\phi = \frac{\text{no. adsorbed molecules}}{\text{no. carbon atoms}} = \frac{m_c}{m_{ads}} \left[\left(\frac{f_0}{f_{res}} \right)^2 - 1 \right]$$

where m_c and m_{ads} are the molecular weights of carbon and adsorbate, and f_0 and f_{res} are respectively the resonance frequencies of the bare nanotube and of the nanotube plus adsorbate. So, by tracking the resonance frequency in mixing current at constant gate voltage and temperature, we obtained adsorption isotherms, ϕ versus P , see Fig. 2.7.

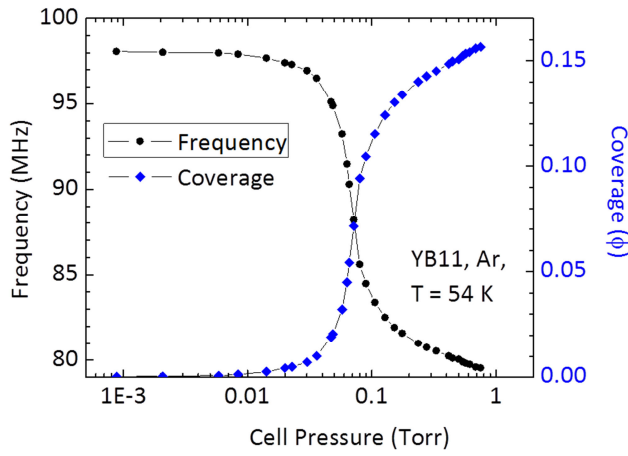


Figure 2.7 Resonance frequency (f_{res}) and adsorption (ϕ) isotherms of the device YB11 versus Ar pressure, at $T = 49$ K.

2.4 Conductance Measurement

As mentioned in chapter 1, several experiments had shown that the electrical conductance of carbon nanotubes is affected by gases adsorbates on their surface. Here I compare the mass adsorption with the conductance changes under very well controlled pressure and temperature conditions.

G-V_g measurement :

The conductance $G = I_{sd}/V_{sd}$ is measured using a low frequency (typically 740 Hz) AC source-drain excitation V_{sd} comparable with $k_B T/e$ (typically between 0.5 to 2 V divided by a voltage divider by a factor of 1000). Measuring the conductance versus the gate voltage with the temperature and $V_{source-drain}$ being constants, we often sweep the gate voltage within the range $-4 \text{ Voltage} < V_g < 4 \text{ Voltage}$. A sketch of the conductance measurement setup is shown as Fig. 2.8.

The $G-V_g$ measurement shows us some properties of the devices, including whether the devices are metal, or semiconductor, small gap semiconductor, or big gap semiconductor. Sometimes it also tells us whether the devices are well connected to the source and drain or not.

We measure the $G-V_g$ at different temperatures, in vacuum or with different gas pressure. The $G-V_g$ dependence will be modified by the adsorbates shown in Fig. 2.9.

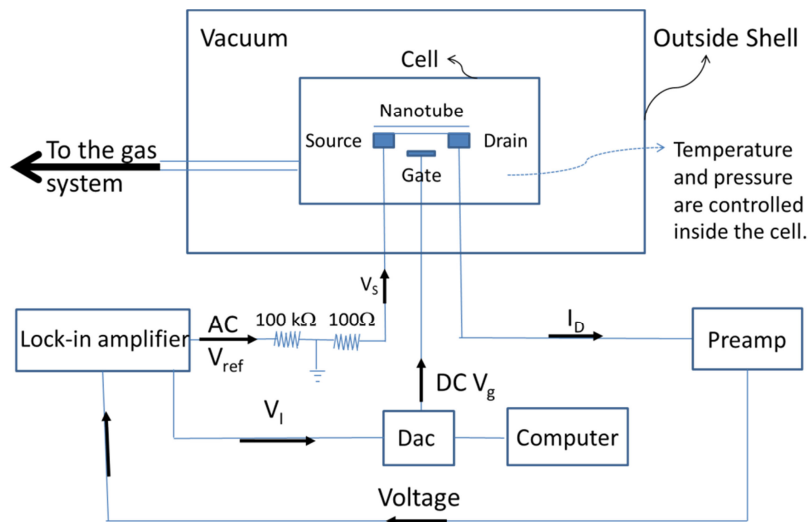


Figure 2.8 - A block diagram of the conductance measurement setup

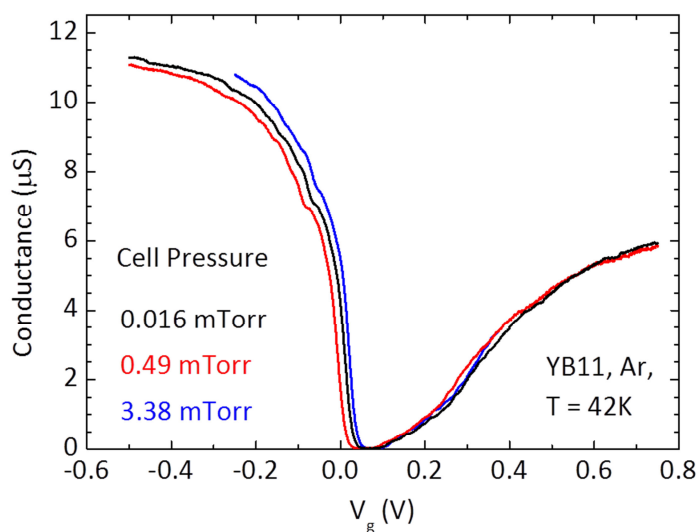


Figure 2.9 - The conductance versus gate voltage of device YB11 at three constant Ar pressures, 0.016 mTorr, 0.49 mTorr, and 3.38 mTorr, at $T = 42\text{ K}$

Conductance isotherms measurement:

The $G-V_g$ dependence is modified by adsorption. At a constant temperature, and gate voltage, the conductance changes with adsorption.

We fix the gate voltage where a sharp slope happens in the $G-V_g$ diagram, add in or pump out gas slowly, and record the conductance versus gas pressure. We take about 3 to 30 measurements per second depending on the speed of the gas flow and the time constant chosen for the lock-in amplifier. The

output AC source-drain voltage is also typically between 0.5 to 2 V divided by a voltage divider by a factor of 1000.

We measure the continuous conductance isotherms by letting the gas pressure decrease or increase slowly and continuously as Fig. 2.10.

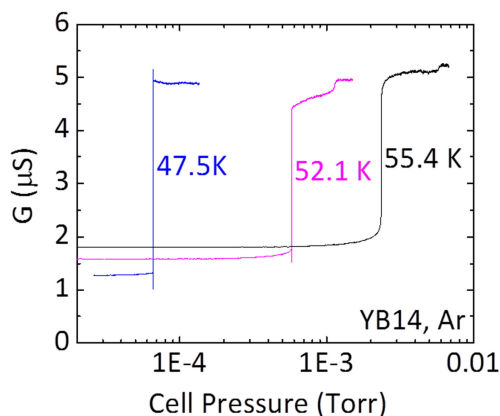


Figure 2.10 – Three conductance, Ar isotherms measured on SWNT YB14 at $T = 47.5, 52.1$, and 55.5 K

We also measure discontinuous conductance isotherms by letting the gas pressure change by small steps. The discontinuous measurements are taken often when we are taking the coverage frequency measurements at the same time, so that we can have the conductance and coverage at exactly the same pressure and almost the same amount of gas adsorbed shown as Fig 2.11.

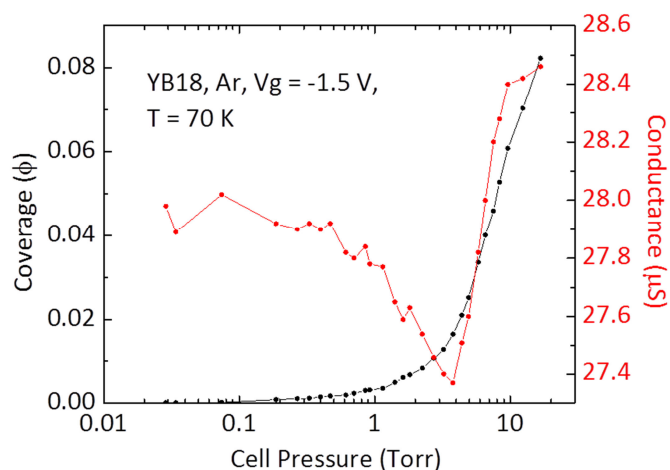


Figure 2.11 – Adsorption and conductance isotherms of device YB18 at $V_g = -1.5$ V, $T = 70$ K, with discretized, equilibrium pressure steps

Chapter 3. Results

Many experiments were performed on coverage isotherms (ϕ -P, with V_g fixed), conductance isotherms (G-P, with V_g fixed), and conductance versus gate voltage (G- V_g , with temperature fixed) for different pressures of Ar and Kr on most devices. Some other gases, for example He, Xe, O_2 , etc., were measured with some devices, with a limited amount of data acquired.

In this section, I will present an overview of the results. The actual complete set of data is in the Appendixes.

3.1 Devices with Isotherms

Our single-walled carbon nanotube devices are referred with YB (Yocto-balance, $1 \text{ yg} = 10^{-24} \text{ g}$) followed by a number. In fact, the mass sensitivity of the coverage measurement is in the range of about $10 \sim 100$ atoms, roughly of the order of 100 yg .

Following Z. Wang's measurements on devices YB1 to YB8, I studied the adsorption on the single-walled carbon nanotubes, YB10 (He^4), YB10a (Ar and Kr), YB11 (Ar, Kr, and O_2), YB12 (Kr), YB14 (He^4 , Ar, Kr, and Xe, only conductance was measured, there is no coverage data), YB16 (Ar, only conductance was measured), YB18 (Ar and Kr), YB19 (Ar and Kr, only conductance was measured), YB23 (Ar and Kr), and YB24 (Ar and Kr).

All the adsorption ϕ isotherms were measured with discretized equilibrium pressure, see Fig. 3.1 (a), (b), while some of the conductance isotherms were measured with discretized pressure, and some of them with continuous, very slowly changing pressure, see Fig. 3.1 (c), (d). Some discretized conductance isotherms were measured at the same time with the coverage isotherms at the same gas pressures to help correlate G and ϕ features, see Fig. 3.1 (e).

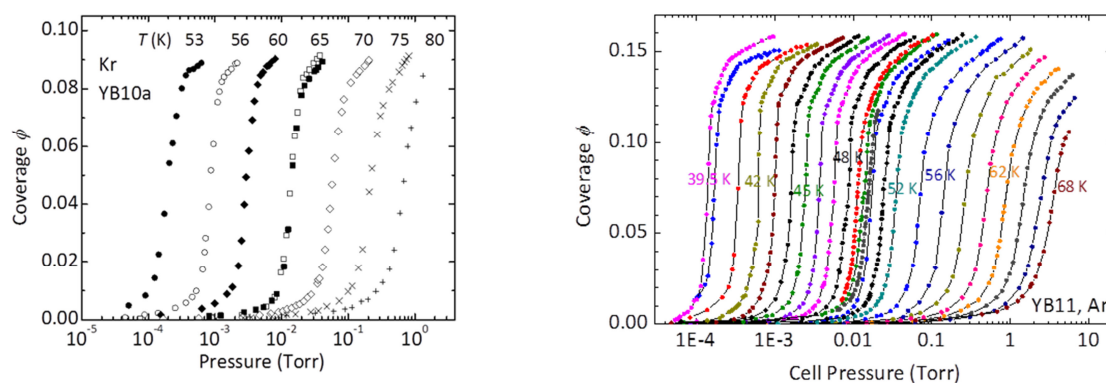


Figure 3.1 (a) - The complete set of Kr adsorption isotherms measured on device YB10a – The complete set of temperatures, from the lowest to highest is, in Kelvin, 53, 56, 60, 65, 70, 75, 80. V_g of the un-filled symbol isotherm at $T = 65 \text{ K}$ was 1.5 V , V_g of the solid symbol isotherm at $T = 65 \text{ K}$ was 4 V , and V_g of all the other isotherms was 3 V .

Figure 3.1 (b) - The complete set of Ar adsorption isotherms measured on device YB11 – The temperatures, from the lowest to highest is, in Kelvin, 39.5, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 49.4, 49.8, 50, 51, 52, 54, 56, 58, 60, 62, 64, 66, 68. The source-drain bias amplitude of the 49 K isotherm was 2 mV, while the bias amplitude of the other isotherms was 5 mV. The difference of the bias amplitude affected the shape of the resonance a little bit, but the coverage calculated based on comparing f_{res} with f_0 did not show significant difference in the adsorption.

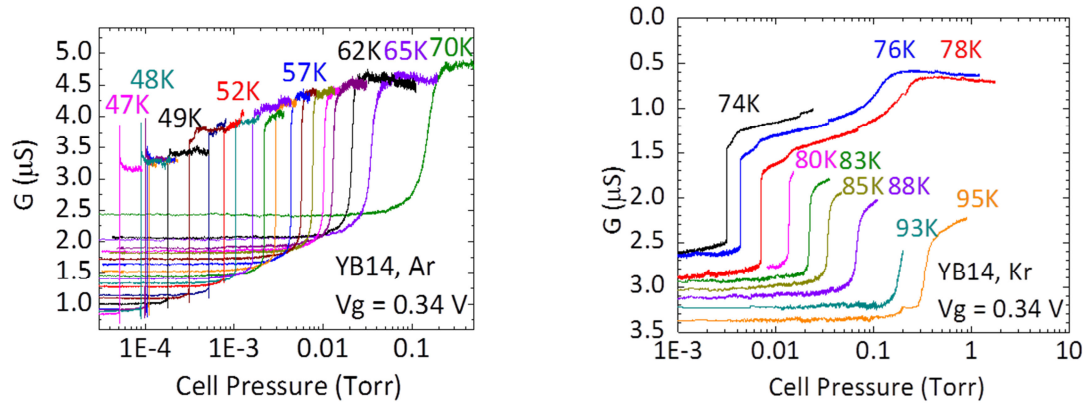


Figure 3.1 (c) - The complete set of Ar conductance isotherms measured on device YB14 – The temperatures, from the lowest to highest are, in Kelvin, 47, 48, 48.163, 48.256, 48.455, 49, 50, 52, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 65, 70. The gate voltage and the source-drain bias voltage were both fixed.

Figure 3.1 (d) - The complete set of Kr conductance isotherms measured on device YB14 – The temperatures, from the lowest to highest are, in Kelvin, 74, 76, 78, 80, 83, 85, 88, 93, 95. The gate voltage and the source-drain bias voltage were both fixed.

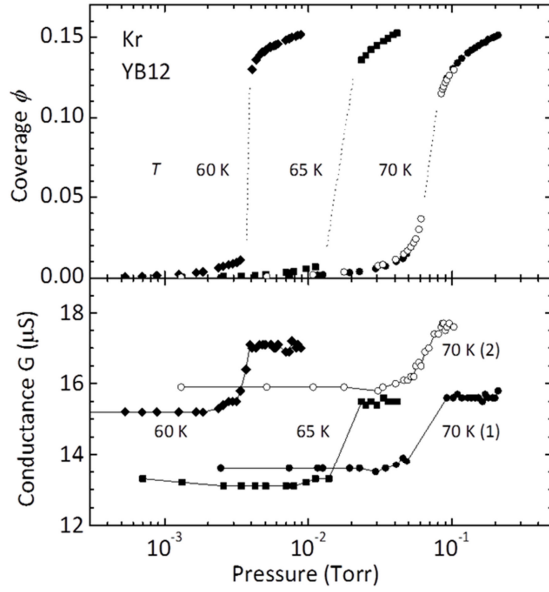


Figure 3.1 (e) - The complete set of Kr coverage and conductance isotherms measured on device YB12 – The temperatures, from the lowest to highest are, in Kelvin, 60, 65, 70. The coverage and conductance isotherms were measured together with the same equilibrium pressures. We measured isotherms at $T = 70$ K twice. Observing the two ϕ and two G isotherms at 70 K, we found that though the conductance was shifted between the two measurements, the coverage remained the same.

In most cases we used the same source-drain bias and the same gate voltage for all the isotherms on each device. Occasionally, the source drain bias or the gate voltage was changed in some adsorption measurements. The data might be affected a little bit, but there was no significant difference in the coverage comparing two isotherms at the same temperature, see 3.1 (a), (b).

There is a large riser in each isotherm, no matter whether it is a coverage isotherm or a conductance one. The pressure where the large risers happen depends on the temperatures of the isotherms. For each SWNT, the pressure of a large riser of an isotherm is higher if the temperature is higher. Roughly speaking, for one nanotube, the difference between the logarithm of the pressures of the isotherms is about the same if the temperature difference between the isotherms is the same, see Fig. 3.1 (a), (b), (c), (d), (e).

When the source voltage amplitudes used are similar for the coverage and conductance isotherms, the pressure where the large risers happen will be about the same for the two types of isotherms on the same device at the same temperature, see Fig. 3.1 (e).

For different devices, the pressures of the risers may have a big difference for isotherms at the same temperatures. The maximum coverage of adsorption on the SWNTs at the saturated gas vapor pressure

of the gas used can also be very different amongst devices, see Fig. 3.2 (a), (b). The large risers at comparable pressure for SWNTs YB3 and YB8 occurred at higher temperatures than for YB10a, YB11, YB12 and YB18. YB3 and YB8 also achieved higher $\phi_{\max}$ than other devices at the saturated pressures.

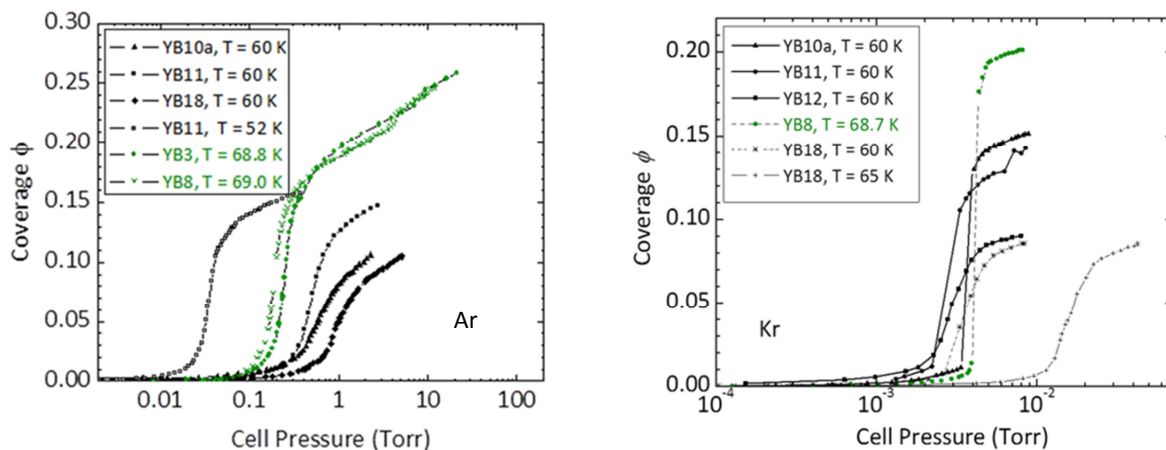


Figure 3.2 (a) - A comparison of Ar isotherms on Class 1 devices (YB3 at 68.8K and YB8 at 69.0K) and isotherms on Class 2 devices (YB10a and YB18 at 60K and YB11 at 52 and 60K).

Figure 3.2 (b) - A comparison of Kr isotherms on a Class 1 device (YB8, 68.7K) and several Class 2 devices (YB10a, YB11, YB12 at 60K) and YB18 (60K and 65K).

Based on the measurements, our SWNTs seem to fall into two classes. Device YB14 looks like belong to the same class of YB3 and YB8 (the last two devices were measured by Z. Wang) (79) (80), while other devices, YB10 to YB24, except YB14, belong to another class.

3.2 Class 1 devices: YB3, YB8, and YB14

Devices, YB3 (ϕ is measured for Ar and Kr), see Fig. 3.3 (a), and YB8 (ϕ is measured for Ar and Kr), see Fig. 3.3 (b), were measured in the liquid nitrogen cryostat by Z. Wang. (80) SWNT YB14 (G is measured for He, Ar, Kr, and Xe), see Fig. 3.1 (c), (d) was measured using the cryocooler.

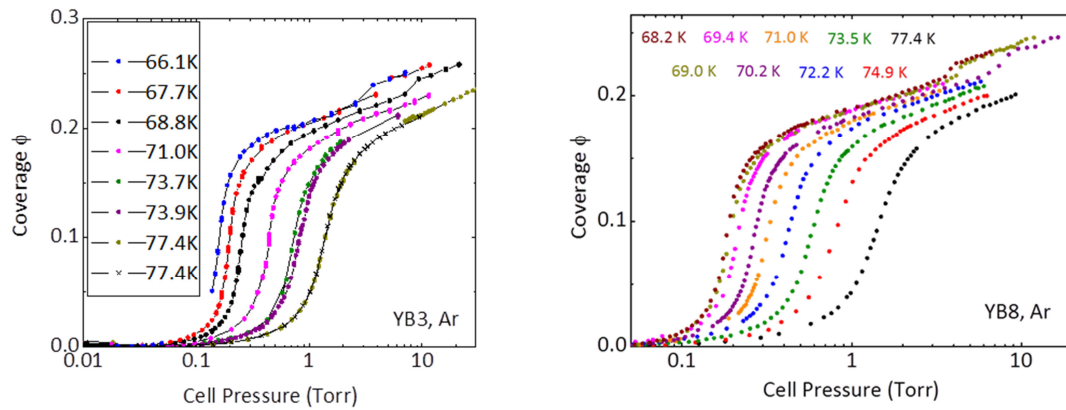


Figure 3.3 (a) – Ar adsorption isotherms on device YB3 – All isotherms were measured at T larger than the 2D L-V critical temperature. Three isotherms (66.1 K, 67.7 K, and 68.8 K) showed the solid formation step at $\phi \sim 0.22$. Data was taken by Z. Wang. (79) (80)

Figure 3.3 (b) – Ar adsorption isotherms on device YB8 – All isotherms were measured at T larger than the 2D L-V critical temperature. Three isotherms (68.2 K, 69.0 K, and 70.2 K) showed the solid formation step at $\phi \sim 0.22$. Data was taken by Z. Wang. (79) (80)

Among these three devices, no matter whether they were coverage or conductance isotherms, the slope of the large risers increased as the temperature decreased. When the temperature was low enough, the large riser was too sharp to be resolved with the pressure intervals used. They showed clear 2d phase coexistence regions for Ar, Kr, and Xe. The large risers of the isotherms occurred at lower pressures than for devices of another class for the same temperatures, see Fig 3.2 (a), (b).

A full dense monolayer coverage is possible before reaching the 3d saturated vapor pressure of the adsorbates. The maximum coverage of Ar and Kr on YB3 and YB8 was comparable to the density of the monolayer planes of the same gases adsorbed on graphite, with the consideration of the larger diameter (area) of the monolayer on a cylindrical surface. We cannot deduce the maximum coverage of Ar, Kr and Xe on YB14 since no resonance measurements were possible with this device, and we don't know the relationship between the variations of the conductance of the nanotube and the surface coverage. A number of factors, for example scatters, need to be considered for conductance changing (82) (83) (84). Note that as coverage increased, sometimes the change in conductance reversed direction.

In the Ar and Kr isotherms of these three devices, we see clear and smaller steps following the large risers. The coverage, $\phi \sim 0.22$, where the small steps happened in the Ar isotherms of YB3 and YB8 corresponds to the coverage of the 2d fluid-solid coexistence region of Ar adsorbates on graphite. Naturally, we interpret the large risers as the vapor-liquid phase transitions (or totally fluid if there is no point in the isotherm where the slope is infinite), and the smaller steps as the liquid-solid transitions.

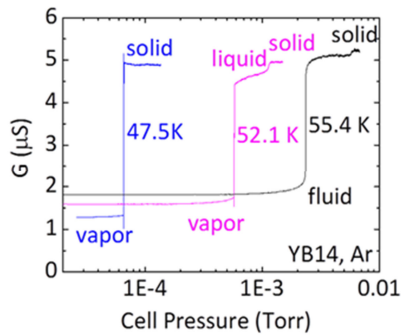


Figure 3.4 – Three conductance, Ar isotherms on device YB14 at $T = 47.5 \text{ K}$ ($T < T_{\text{triple}}$), 52.1 K ($T_{\text{triple}} < T < T_{\text{critical}}$), and 55.4 K ($T > T_{\text{critical}}$). A clear, small step indicating a liquid-solid or fluid-solid transition was observed in isotherms with $T > T_{\text{triple}}$. A spike was seen at the vapor side of the vapor-liquid transition, and there was a spike at both the vapor and solid side of the vapor-solid transition.

A comparison of Kr adsorption amongst these three devices is shown in Fig. 3.5. We show one isotherm near 77K for each Class 1 device. The YB14 conductance isotherm is matched with the coverage isotherms at the small step at $\phi \sim 0.18$ in YB8 (taken from Fig. 1 of Lee et al.). (85)

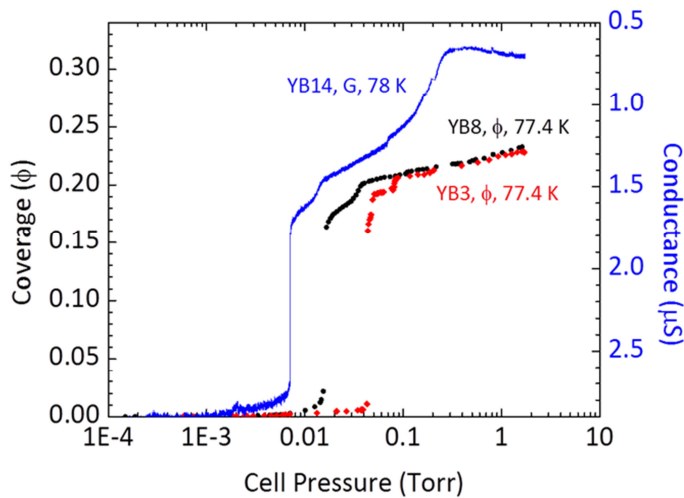


Figure 3.5 - A comparison of Kr adsorption amongst devices YB3, YB8, and YB14. One isotherm near 77K is shown for each device. The YB14 conductance isotherm is matched with the coverage isotherms at the small step at $\phi \sim 0.18$ in YB8.

Looking at the three isotherms for more detail, the pressures of the large risers were a little different among them. It seems that YB8 and YB14 devices were similar: Both of the large risers were followed by

a smooth small step, and the small steps had almost the same shape. On the other hand, the Kr isotherm at 77.4 K on YB3 has a vertical jump from small ϕ up to $\phi \sim 0.17$, close to the commensurate density of Kr/graphite, and was followed by second and third smaller vertical steps at increasing pressures before reaching $\phi_{\max} \sim 0.23$ at P_{vapor} .

At the lowest temperatures, device YB14 showed strong Coulomb blockade oscillations in its conductance as a function of V_g . Furthermore, the conductance oscillations shifted markedly with ^4He adsorption. Fig. 3.6 (a) shows how the G - V_g data related to ^4He exposure at $T = 7.5$ K. The conductance was measured with respect to the gate voltage while ^4He was pumped out of the cell. The conductance peak shifted to the negative-gate-voltage side as the ^4He pressure decreased. Fig. 3.6 (b) shows how a peak of conductance of device YB14 shifted as a function of ^4He pressure at several different fixed temperatures.

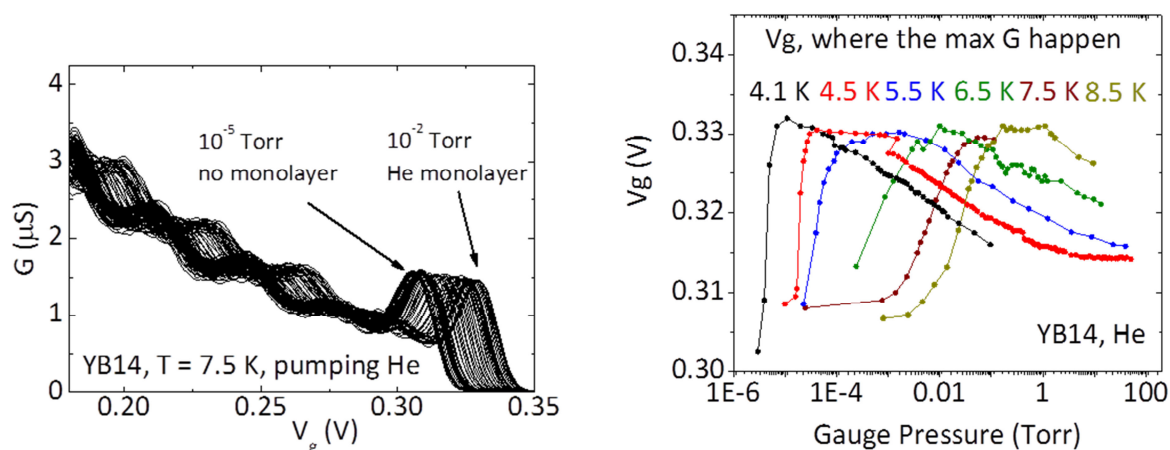


Figure 3.6 (a) - Coulomb blockade oscillation of the conductance of the YB14 device and their dependence on adsorbed ^4He at $T = 7.5$ K

Figure 3.6 (b) - ^4He $V_g^{(\text{maximum})}$ isotherms of device YB14 measured by tracking one of the Coulomb peaks shifts

The Xe conductance isotherms on YB14 showed large risers, see Fig. 3.7. When the temperature was low enough, the large riser were too sharp to be resolved with the pressure intervals used similar to what we see in the Ar and Kr isotherms on the same device. These isotherms show a similarity between the Xe/YB14 and Xe/graphite phase diagrams.

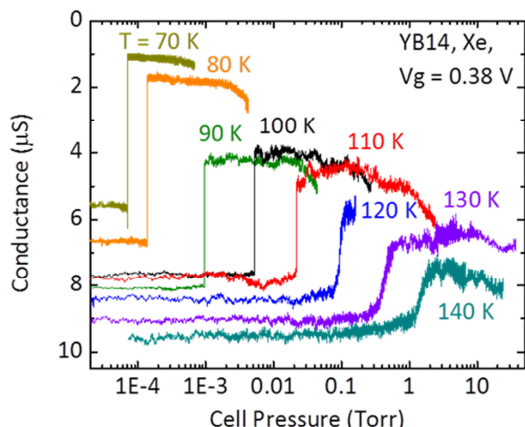


Figure 3.7 - The complete set of conductance Xe isotherms measured on device YB14 – The temperatures, from the lowest to highest, are 70, 80, 90, 100, 110, 120, 130, and 140 K.

3.3 Class 2 devices: YB10, YB10a, YB11, YB12, YB16, YB18, YB19, YB23, and YB24

Devices YB10 (ϕ is measured with ^4He), YB10a (ϕ and G are measured for Ar and Kr), YB11 (ϕ and G are measured for Ar and Kr), YB12 (ϕ and G are measured for Kr), YB16 (G is measured for Kr), YB18 (ϕ and G are measured for Ar and Kr), YB19 (G is measured for Ar and Kr), YB23 (ϕ and G are measured for Ar, and G is measured for Kr), YB24 (G is measured for Ar and Kr, only one ϕ isotherms is taken with each gas) look like belong to another class; we call it Class 2. Isotherms on these devices were measured using the cryocooler.

Adsorption isotherms of Kr on YB10a are shown in Fig. 3.1 (a), adsorption isotherms of Ar on YB11 are shown in Fig. 3.1 (b), and a comparison between adsorption and conductance isotherms of Kr on YB12 can be seen in Fig. 3.1 (e). For the complete data, please see the Appendix.

The pressures where the large risers happened in the isotherms of class 2 devices were higher than those on class 1 devices by about 1 or 2 orders of magnitude at the same temperatures. The maximum possible before reaching the saturated vapor pressure of the adsorbates on the class 2 devices was lower than what was observed for YB3 and YB8. Some comparisons of isotherms of these two classes of devices can be seen in Fig. 3.2 (a), (b). There was no clear feature following the large risers indicating the liquid-solid transition.

Except for YB11, YB12 and YB16, the slopes of the large risers of all the other class 2 SWNTs looked more like constants, and were always finite even at very low temperatures. The slope of the large risers increased with ϕ_{max} . Broadening of an L-V step (lack of a perfect vertical step) is conventionally related to inhomogeneity or finite size effects. (86)

For YB11, the slopes of the large risers for the Ar isotherms increased more and more slowly as the temperature decreased, and did not become vertical at 39.5 K, the lowest temperature measured. For

YB12, the slope of the risers of the Kr isotherms seemed to increase as the temperature decreased, but did not reach infinite at 60 K, the lowest temperature we measured, see Fig. 3.1 (e). The isotherms were obtained only at three temperatures, and the resonance disappeared in the middle of the large risers, so, it's difficult to tell whether the slope increased more slowly or not at the lower temperature. For YB16, we do not have adsorption isotherms, but the slope of the risers of the conductance isotherms increased as the temperature decreased, see Fig. 3.8. We are not sure whether the large risers in the YB16 conductance isotherms became vertical or not at 42 K because of the noise in the data. It seemed that the slope increased more and more slowly as the temperature decreased, like YB11.

YB12 and YB16 followed other properties of class 2 devices: no clear features indicating the liquid-solid state, the maximum coverage of YB12 measured being lower than what for YB3 and YB8, and the higher pressures required for the isotherms' risers than class 1 devices (though for YB16 the pressures are not as high as for other class 2 devices.) There was a feature at the region $0.13 < \phi < 0.15$ in Ar isotherms of device YB11, see Fig. 3.1 (b). The feature was reproducible, but not as significant as the small steps showing the 2D S-L transition in isotherms of YB3, YB8, and YB14. Furthermore, the ϕ is much lower than expected for an Ar fluid-solid transition, which should be around $\phi \sim 0.22$ (or larger for nanotubes with $R_0 < 1\text{nm}$).

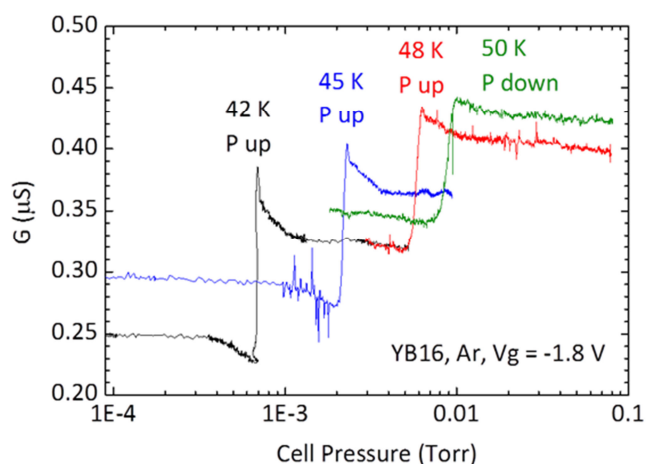


Figure 3.8 - The set of Ar conductance isotherms measured on device YB16 – The temperatures, from the lowest to highest are, 42, 45, 48, and 50 K. When the 50 K isotherm of YB16 was measured, Ar was pumped out of the cell. When the other three isotherms were measured, Ar was added into the cell. There is an expected shift in pressure due to the impedance of the dosing tube.

We measured $G-V_g$ of some devices at different temperatures, in vacuum or with different gas pressure. The changes in G were subtle, but when they can be combined with frequency measurements used to determine the coverage, complete phase diagrams and subtle features of the adsorbate phases can be observed and correlated to coverage, see Fig. 3.9 (a), (b), (c).

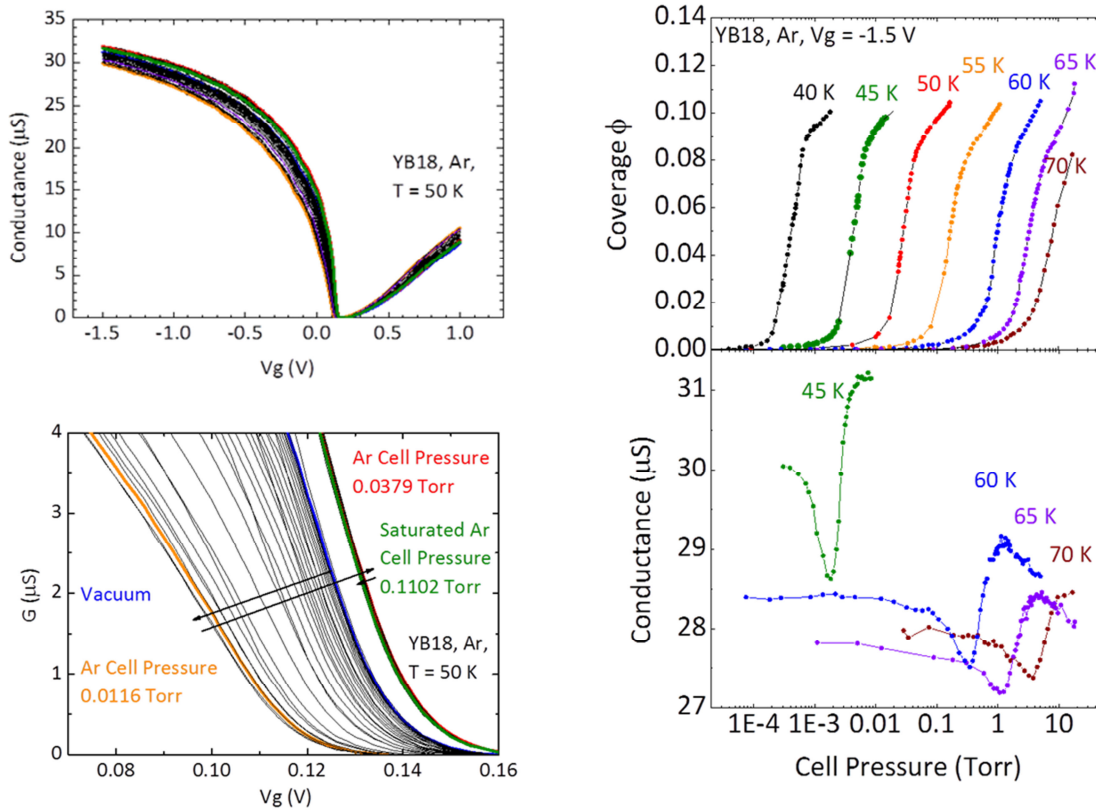


Figure 3.9 (a) – $G-V_g$ of device YB18 at $T = 50$ K with many different equilibrium pressures of Ar

Figure 3.9 (b) – Enlarge part of Figure 3.9 (a) – The lines with the blue, orange, red, and green colors represent the $G-V_g$ under the following conditions, in vacuum, with Ar pressure 0.0116 Torr, 0.0379 Torr, and 0.1102 Torr.

Figure 3.9 (c) – Adsorption and conductance isotherms of device YB18 with Ar at $V_g = -1.5$ V

3.4 Middle points of the large risers in the isotherms

In this section, we plot on a $\log P$ vs. $1/T$ graph the middle points of the large risers in the isotherms, and also the middle points of the small steps following the large risers if they exist, for the two classes of devices, from YB10 to YB24 plus YB3, and YB8, comparing them to $\log P$ vs. $1/T$ of the phase transition points of adsorbates on graphite and saturated vapor pressure of the gas used.

Temperature-pressure summary of the large risers in Ar isotherms on SWNTs

Fig. 3.10 shows the middle points of the large risers and small steps in the Ar isotherms, points of the positions of the phase transition of Ar on graphite (26), and the Ar 3d transition vapor pressure []. The measurements on YB14, YB16, YB19, and YB24 were obtained purely from conductance isotherms.

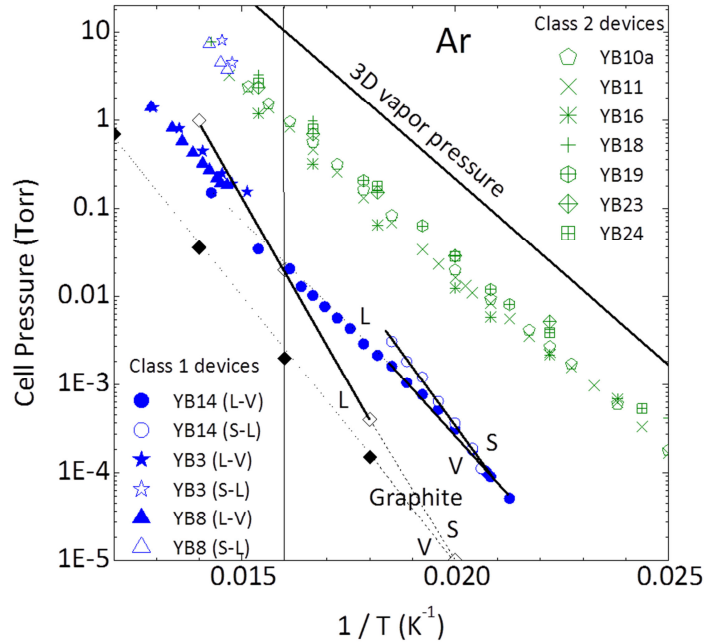


Figure 3.10 – Temperature-Pressure summary of the middle points of the large and small risers in the Ar isotherms of devices – The blue marks present data of Class1 devices YB3, YB8, and YB14, while green marks present data of Class2 devices, YB10a, YB11, YB15, YB16, YB18, YB19, YB23, and YB24. The data for Ar on graphite are plotted with black marks, full symbol presenting L-V transition, and open symbol presenting SOL transition, see (26).

The devices fall into two classes, as shown in Sections 3.2 and 3.3. There were clear phase transitions (large jumps at low P and smaller steps at higher P on the same isotherm) of Ar adsorbates on YB3, YB8, and YB14, resembling the phase transitions on graphite. We have drawn straight lines representing the V-L and L-S phase boundaries for YB14 and graphite.

On the other hand, YB10a, YB11, YB15, YB16, YB18, YB19, YB23, and YB24, without vertical transitions, are presented with the middle points of the large risers in isotherms. The behaviors of the Ar adsorbates of these devices were similar to each other, with higher vapor pressures on adsorption, translating to a lower finite coverage isosteric heat. No clear small steps following the large risers were found.

Temperature-pressure summary of the large risers in Kr isotherms on SWNTs

Fig. 3.11 shows the middle points of the large risers and small steps in the Kr isotherms, the positions of the V-CS (commensurate solid) phase transition of Kr on graphite [], and the Kr 3d V-S transition vapor pressure []. The measurements on YB12, YB14, YB19, YB23, and YB24 were obtained purely from

conductance isotherms. We do not distinguish between commensurate and incommensurate solid (IS) in this figure.

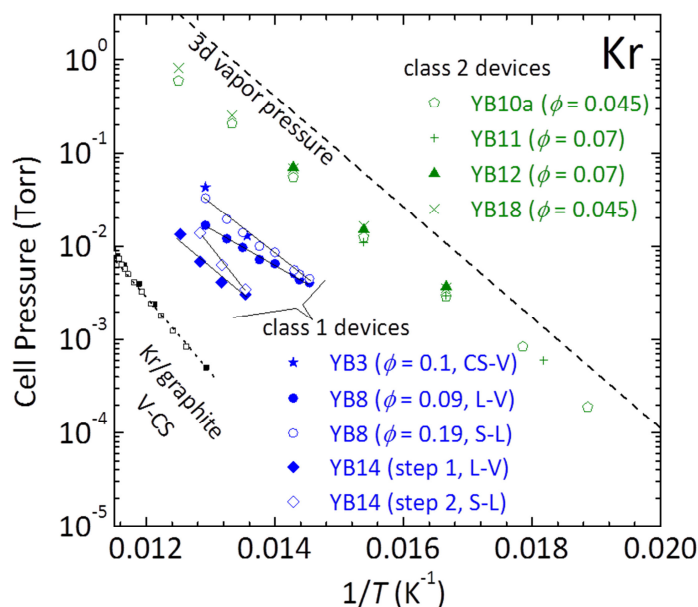


Figure 3.11 - Temperature-Pressure summary of the middle points of the large risers in the Kr isotherms of devices – The blue marks present data of devices YB3, YB8, and YB14, while green marks present data of other SWNTs, YB10a, YB11, YB12, YB18, YB19, YB23, and YB24. The data of Kr on graphite are plotted with black marks.

Consistent with what we found in the T-P summary Fig. 3.10 for Ar, the devices again appeared to fall into two classes. There were clear phase transition jumps (large vertical step at low P and smaller steps at higher P on the same isotherm) of Kr adsorbates on YB3, YB8 and YB14, resembling the phase transitions on graphite like the behavior of Ar adsorbates. YB8 and YB14 appeared to have both L-V and S-V transitions, and certainly different than for Kr/graphite.

YB10a, YB11, YB12, YB18, YB19, YB23 and YB24, without vertical transitions, are presented as the middle points of the large risers in isotherms. The behaviors of the Kr adsorbates of these devices were similar to each other, with higher vapor pressures on adsorption, translating to a lower surface isosteric heat at finite coverage. No clear small steps following the large risers were found. Extrapolating the line of the middle points of the large risers in the isotherms of these devices to lower T (higher $1/T$), we see that they converge to the 3d vapor pressure line. It indicates that the coverage on these devices is only partially full which is consistent with the low maximum coverage of the isotherms.

Temperature-pressure summary of the large risers in He isotherms on SWNTs

Fig. 3.12 shows the middle points in the ^4He isotherms, points of the positions of the phase transition of ^4He on graphite (1), and the ^4He 3d transition vapor pressure. The measurements on YB14 were obtained purely from conductance isotherms.

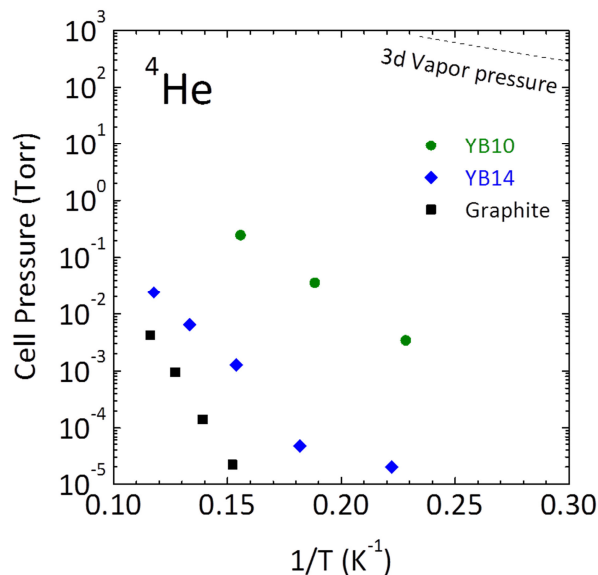


Figure 3.12 - Temperature-Pressure summary of the ^4He isotherms of devices – The blue marks present data of device YB14, while green marks present data of YB10. The data of ^4He on graphite are plotted with black marks.

The ^4He isotherms on device YB10, see Fig. A2.30 in the Appendix, did not reach the high enough coverage or low enough temperature needed to observe a phase transition. There were no large risers shown in the isotherms. In Fig. 3.12, we marked the middle points of the YB10 ^4He isotherms. Regarding YB14, we tracked the shift of the Coulomb blockade peaks of conductance in $G-V_g$ with respect to the ^4He pressure exposure, and marked the ^4He pressure of the middle points of the big shift of the conductance peaks.

In Fig. 3.12, we see that the ^4He pressures required for YB14 were higher than for graphite, but much lower than for YB10, at the same temperatures. Also, in Fig. A2.30, the three isotherms looked like three parallel lines. So, we interpreted that nanotube YB10 belonged to class 2 of the SWNTs.

3.5 Summary of the comparison of the devices

Here is the table of the summary of the results of the (possible) two classes of SWNTs.

	Class 1	Class 2
Devices	YB3, YB8, and YB14	YB10, YB10a, YB11, YB12, YB16, YB18, YB19, YB23, YB24

Pressures of the middle points of the large risers in isotherms	Lower (lower than class 2 devices, but higher than graphite)	Higher (Higher than class 1 devices)
Slopes of the large risers	Increased as the temperature of isotherms decreased	Almost constant with respect to the temperature, except YB12 and YB16
Small steps following the large risers	Exist and are clear	No clear and convincing ones exists
Maximum coverage	Comparable to the maximum coverage on graphite, with the consideration of the radius of the SWNTs	Lower
T-P summary of the large risers and small steps	Resembling what for graphite, but with lower pressure required	Different with graphite, just a straight line, converging to the 3d vapor pressure line as the temperature decreases. (The converging is clear for Kr data, but not so significant for Ar data.)

Chapter 4. Discussion

In this chapter, we discuss and analyze the data. Based on the isotherms of the devices, we talk about the diameters of the SWNTs, the 2D critical and 2D triple points of the adsorbates on the surfaces of the nanotubes, the isosteric heat and binding energy of the noble gases on them, and the 2D latent heat of Ar and Kr on SWNT YB14.

4.1 Diameters of the nanotubes

The simplest model of a single-walled carbon nanotube consists of a uniform cylinder of a material of negligible thickness and radius R_0 with continuous uniform 2d density of basal plane graphite. If adsorption were to proceed in a similar way as it happens on graphite and at the formation of the 2d solid the adsorbed monolayer were to have the same density as on graphite at a distance d above the nanotube, then the nanotube monolayer coverage (ϕ) will be larger than the one on graphite (ϕ_{gr}) by

$$\phi = \phi_{gr} [1 + (d/R_0)] \quad (3)$$

due to the larger radius of the physisorbed gas cylinder. For Ar/gr at 40 K neutron diffraction results give a nearest neighbor separation $a_{nn} = 0.398$ nm (87) and LEED at 42.5 K gives $a_{nn} = 0.394$ nm (88), both expanded with respect to the (111) planes of 3d Ar at 40 K, $a_{nn} = 0.383$ nm [Pollack]. At the 2d triple point melting of Ar/gr, Taub et al measured $a_{nn} = 0.406$ nm, or $\phi_{gr} \sim 0.184$. Calculations using the smooth substrate approximation give $d_{Ar} \sim 0.34$ nm [Kim et al.]. With these figures we can estimate the diameters of YB3 and YB8, for which the top of the incommensurate solid transition in the 77.4 K isotherms occurs at coverage of $\phi \sim 0.25$ and 0.225 , respectively. The estimates are $R_0 \sim 1$ nm for YB3 (2 nm diameter) and $R_0 \sim 1.5$ nm (3 nm diameter) for YB8.

We use these diameters to estimate the density of 2d Kr at the top of the coverage steps at $\phi = 0.215$ and 0.192 respectively for YB3 and YB8. The smooth substrate approximation for the Kr/nanotube adsorption potential gives $d_{Kr} \sim 0.36$ nm [Kim et al]. Thus for YB3, $\phi_{gr} = 0.158$ and for YB8, $\phi_{gr} = 0.155$, quite similar, which translate to a 2d uniform density $n \approx 5.9$ nm⁻² or $a_{nn} \sim 0.44$ nm. This a_{nn} is somewhat large; at 80 K, $a_{nn} \sim 0.41$ nm for the (111) planes of 3d Kr, with a surface density of 6.9 nm⁻² [Pollack]. Kr on graphite though forms a commensurate solid with $a_{nn} \sim 0.425$ nm, which pre-empts the L-V transition and generates a complex phase diagram at high densities and these temperatures, so the exact 2d S-L behavior is not well known. The estimate may not be too far off. The isotherms of Kr/YB3 and Kr/YB8 at 77.4 K were measured all the way up to 1.75 Torr, the saturated vapor pressure of Kr at this temperature. For YB8, the top coverage was $\phi \sim 0.243$. If $\phi = 0.155$ corresponds to $n = 5.9$ nm⁻² density, then $\phi = 0.243$ will give a 2d density at maximum coverage of $n \sim 7.2$ nm⁻², still higher than the crystalline planes of Kr. The same estimate on YB3 gives maximum density of 6.4 atoms per square nanometer.

It is obvious that this analysis cannot be applied to Class 2 devices. The maximum ϕ on these devices is less than the L-S transition coverage observed for Class 1 devices. Reduction in diameter of the nanotube produces lower binding energies, but it will generate larger values of $\phi = \frac{N_{adsorbed}}{N_{carbon}}$ since when d becomes equal to R_0 the adsorbing area will be twice the nanotube area.

4.2 2D Critical Points and 2D Triple Points

The inverse slopes of the larger riser of the YB3/Ar isotherms extrapolated to zero at a likely 2d L-V critical point, located near 54 K. This is similar to the location of $T_c(2d)$ of Ar/graphite determined by Chan et al. (25). The data of Ar/YB8 can be superimposed on the YB3 data, thus the same conclusion is valid. Both YB3 and YB8 isotherms were measured in a liquid N₂ cryostat where the T_c range could not be explored.

Fortunately, conductance isotherms on Ar/YB14, the device apparently quite similar to YB8, installed in the cryocooler, were able to do so. Fig. 3.1 (c) shows the complete set of Ar/YB14 isotherms. Although no resonance observation was possible on this SWNT, features of the conductance isotherms could be matched to those of the YB3 and YB8 isotherms and thus we were able to extract a considerable amount of information from them. The adsorbed Ar film, as the temperature decreased from 70 K, underwent a series of phase transitions. The inverse slopes at the middle point of the large riser observed in YB14 went to essentially zero near 54K, with vertical isotherms below this temperature, see Fig. 3.4 and Fig. 4.1 (a). And the small and the large vertical steps merged at 48 K, see Fig. 3.4 and Fig. 4.1 (b). We thus claim that Ar/YB14 has a L-V critical point and a S-L-V triple point, both at essentially the same temperatures observed by Chan et al. (25). This is the first time that this region of the phase diagram of monolayer Ar (on graphite surfaces) has been covered with adsorption isotherms, the main reason that makes it possible being the weaker adsorption energy of Ar on a single wall nanotube.

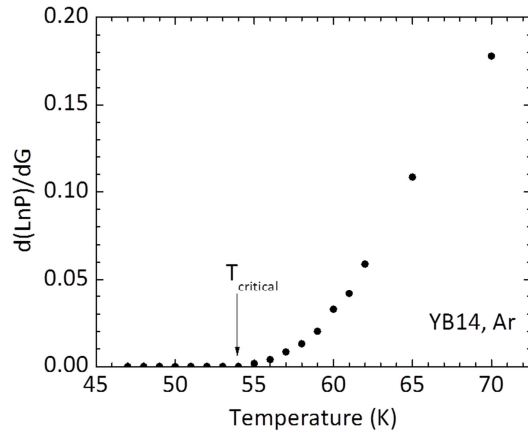


Figure 4.1 (a) – $d(\text{Ln}P)/dG$ at the middle points of large risers of Ar isotherms on YB14

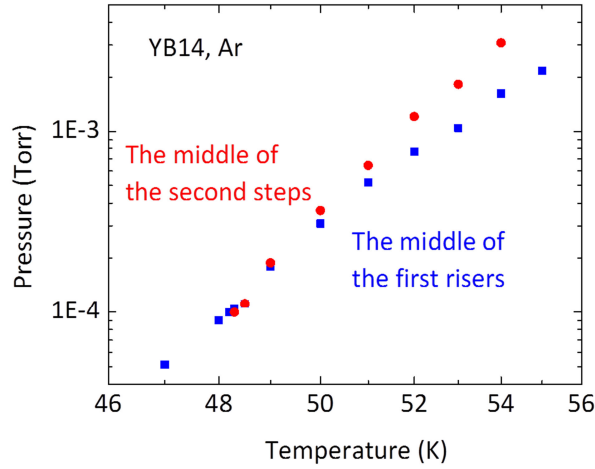


Figure 4.1 (b) – Temperature versus Pressure at the middle points of the first risers (large risers) and the second steps of Ar isotherms on YB14 – The blue squares present the middle points of the large risers, and the red circles present the middle points of the second steps.

For the Kr isotherms, both YB8 and YB14 showed vertical isotherms, consistent with L-V and S-L coexistence regions. The measurements on YB14 indicated that the L-V critical temperature, at which the monolayer lost the vertical step (the end point of an infinite 2d isothermal compressibility), was about 78 K. Although for YB8 we could not go above 77.4 K, its L-V critical point T_{critical} was close to 80 K as estimated from the decrease in the magnitude of the larger vertical step (the coexistence region).

The small step (S-L) and the larger riser (L-V lines) in both YB8 and YB14 converged towards what appeared to be a S-L-V triple point. For YB8, $T_{\text{triple}} \sim 68$ K, slightly below the lowest measured temperature. For YB14, $T_{\text{triple}} \sim 73$ K, also below the lowest measured temperature. From this point of view the differences between these two devices are likely real, but maybe due to inaccuracy in the low P measurements and the thermo-molecular corrections in the two different experimental setups.

For devices of class 2, since there is no clear feature following the large risers indicating the liquid-solid transition, we can't determine the S-L-V triple temperatures, if indeed they exist. Except for YB12 and YB16, the slopes of the large risers of all the other class 2 SWNTs look more like constants, and are always finite even at very low temperatures, so we also cannot determine L-V critical temperatures.

We plotted the normalized inverse compressibility versus reduced temperature for Ar on device YB3, YB8, YB11, and YB14, and for Kr on device YB14, see Fig. 4.1(c). For YB3, YB8, and YB11, resonance (coverage) isotherms were used, the y-axis was defined as $\ln(\phi_c \frac{T}{T_c} [\frac{\partial \ln P}{\partial \phi}]_T)$, where P is the pressure, T is the temperature, ϕ is the coverage in the isotherms, and ϕ_c is set to be 0.075, while for YB14 (both Ar and Kr) conductance isotherms were used, the y-axis was defined as $\ln(\frac{T}{T_c} [\frac{\partial \ln P}{\partial G}]_T)$, with P being the pressure, T the temperature, and G the conductance. The x-axis is the reduced temperature, $\frac{T-T_c}{T_c}$.

In Fig. 4.1 (c) T_c of Ar is set to be 54 K on all the devices, and T_c of Kr is set to be 78 K on YB14. We see that the data of Ar and Kr on YB14 can be fitted by a line with slope being $\frac{7}{4}$, where $\frac{7}{4}$ is the expected slope of the 2D Ising model isothermal compressibility. The logarithm of the inverse compressibility for Ar on YB11 converged to a constant, about 0.79, as the temperature decreased and approached 54 K.

Regarding to discussion and Fig. 4 in Ecke's paper (86), the logarithm of inverse 2D compressibility plotted as a function of the logarithm of reduced temperature from data of adsorbates on an ideal substrate gives a straight line with slope $\frac{7}{4}$, consistent with the Ising model, while for a substrate with binding-energy heterogeneity the logarithm plot gives a curved line with the slope decreasing as temperature decreases. It suggests that the surface of YB14 is an ideal substrate, while YB11 is not.

For the data of Ar on YB3 and YB8, we can't tell much since the temperatures of the isotherms are much higher than the 2D critical temperature of Ar on SWNTs.

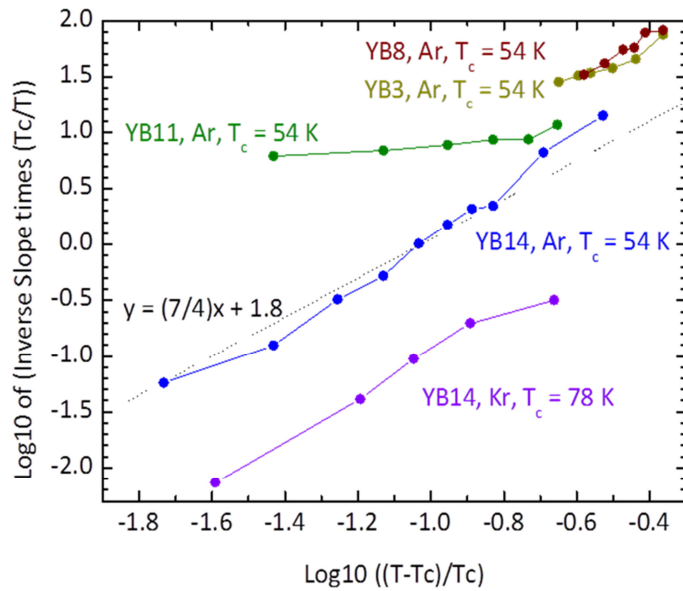


Figure 4.1 (c) - The normalized inverse compressibility versus reduced temperature for Ar on several devices – The data on YB3, YB8, and YB11 was obtained from adsorption isotherms while the data on YB14 was obtained from conductance isotherms as described in the text. Here the critical temperature of Ar is set to be 54 K for all the devices, and the critical temperature of Kr is set to be 78 K for YB14.

4.3 Isosteric Heat and Binding Energy

In this section, we calculate the isosteric heat and binding energy based on the isotherms on our nanotubes. We show the isosteric heat of Ar and Kr on different devices.

Isosteric Heat and Binding Energy

From adsorption isotherms such as those shown in the previous section one can calculate the isosteric (constant coverage) heat of adsorption, which is given (in units of temperature) by

$$\frac{Q_{st}}{k_B} = - \left. \frac{\partial(\ln P)}{\partial(1/T)} \right|_{\phi}$$

at each value of the coverage, see Fig. 4.2. To obtain a value for it, we draw smooth lines through the isotherms and obtain values of P and T for each ϕ at closely spaced values of ϕ , make graphs of $\ln P$ vs $1/T$ and calculate the slope of the resulting lines over the temperature interval where they are approximately linear.

At very low coverage, assuming that the adsorbed 2d gas is an ideal gas,

$$Q_{st} = -\varepsilon_0 + \frac{3}{2}kT,$$

where $-\varepsilon_0$ is the single-atom binding energy to the substrate. By studying the low coverage part of the isotherms, we can calculate the binding energy.

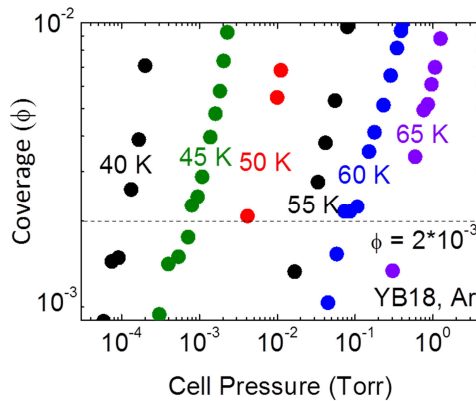


Figure 4.2 – Low coverage region of YB18, Ar, adsorption isotherms, at $T = 40, 45, 50, 55, 60, 65$ K – The thin, dashed line represents the fixed coverage $\phi = 2 \times 10^{-3}$.

Isosteric Heat of Ar

The isosteric heat of Ar on SWNTs is shown in Fig. 4.3 (a) and (b). The coverage scale for YB14, whose steps in conductance isotherms behavior looked consistent and similar to the steps of the coverage isotherms of YB8, had been set to coincide with YB8 at the L-S transition.

The values of Q_{st} at the middle of the large riser and at the middle of the smaller step for Ar on graphite (89) are shown in the figures. The behavior of devices YB3 and YB8 is more similar to graphite than class

2 SWNTs. At zero coverage, the Q_{st} of Ar on all the nanotubes, except device YB23, is considerably lower than on graphite, indicated by an arrow on the left axis.

The isosteric heat of Ar on class 1 devices behaved very differently for $0.2 < \phi < 0.25$ than for $0 < \phi < 0.2$, even for the same SWNT. The additional Q_{st} peak in the narrow range is due to the L-S transition latent heat.

The coverage on class 2 devices did not go higher than 0.2, while maximum coverage of class 1 devices was about 0.25. Roughly speaking, between the region where $0 < \phi < 0.2$, the isosteric heat of Ar on the two classes of SWNTs did not behave very differently. However looking at the isosteric heat for more details, between $0.03 < \phi < 0.17$, Ar on class 1 devices had a Q_{st} between 150 (YB3, YB14) and 300 K (YB8) larger than for class 2 devices. This additional Q_{st} is due, likely, to the 2d L-V latent heat.

In the region $0 < \phi < 0.03$, the isosteric heat of Ar on the two classes of SWNTs behaved similarly. In this low coverage region, except YB23, the isosteric heat of Ar on the devices decreased as the coverage decreased. It indicates that they were clean individual carbon nanotubes. It was difficult to obtain accurate data at very low coverage, but ignoring YB9 and YB23, it is likely that Q_{st} approached 800 ± 50 K as ϕ approaching zero, and there was no systematic difference between the Class 1 and Class 2 devices within the ± 50 K uncertainty of all measurements.

The average of the isosteric heat at $T = 50$ K, $\phi \sim 0$, is about 800 K. The binding energy of Ar, $-\epsilon_0 \sim 800$ K $-\frac{3}{2} \times 50$ K = 725 K or about 30% lower than on graphite (90).

Device YB23 is obviously different. From Fig. 4.3 (b), it's easy to see that at very low coverage ($\phi < 0.04$) Q_{st} rises, and below $\phi = 0.01$ it rises even more. The Q_{st} is reminiscent of the isosteric heat of Ar adsorbed on carbon nanotube bundles, where at very low coverage there are heterogeneous sites, faded over at slightly higher coverages by adsorption on the grooves, between two parallel nanotubes. We have seen in SEM image that occasionally. We have grown two partially joined nanotubes across the trenches that they split. YB23 may have had two joined nanotubes.

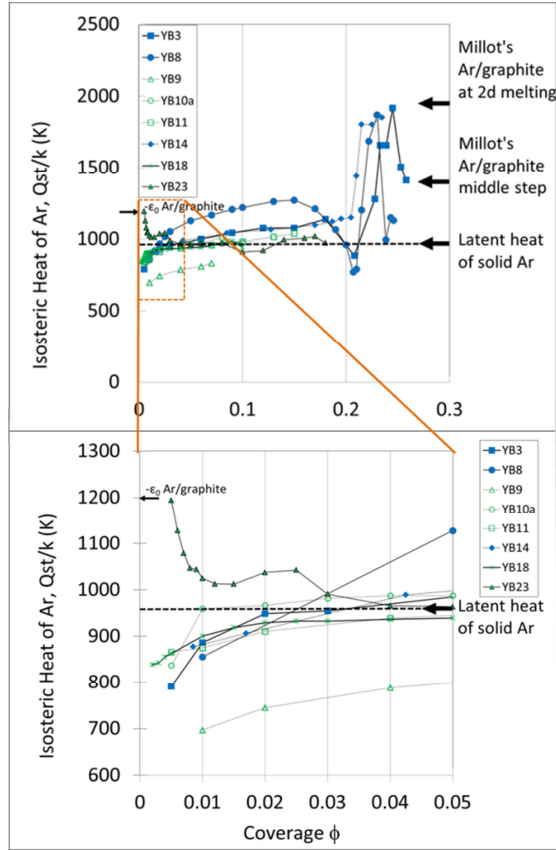


Figure 4.3 (a) - Isosteric heat of Ar calculated as described in text

Figure 4.3 (b) - Enlargement of low coverage region

Isosteric Heat of Kr

Results for Kr are shown in Fig. 4.4 (a), (b), and (c) for all the devices from which more than two isotherms were obtained. The Q_{st} values we obtained are lower than those for Kr/gr. For YB14 (only isotherms at $T = 76$, and 78 K were totally completed, see Fig. 3.1 (d), and used for this calculation), we mapped the steps in G onto the steps in ϕ at the S-L transition in YB8 like what we did for the calculation of the isosteric heat of Ar.

In Fig. 4.4 (a), the isosteric heat of Kr on device YB8 with original data used seems to be too low. We suspect that there was something wrong with the reading of the pressure gauge, for example, the reading was not exactly zero in vacuum. By shifting the zero of the pressure readings for -0.0023 Torr, the isosteric heat of Kr on YB8 will be about constant at $0.05 < \phi < 0.15$, and the result is shown in Fig. 4.4 (b). We see that, in Fig. 4.4 (b), the isosteric heat of Kr on YB8 is roughly the same with the isosteric heat of Kr on YB10a, YB12, and YB18 at $0.02 < \phi < 0.1$, while it is considerably smaller than on YB14 for $\phi > 0.03$, and the L-S transition latent heat of Kr on YB8 (~ 350 K) looks like being only half of YB14 (~ 700 K). Fig. 4.4 (c) shows an enlargement of Fig. 4.4 (b) in the low coverage region.

We tried to find a constant for re-zero the Kr pressure of YB8 data such that the Q_{st} of Kr on YB8 agreed with the Q_{st} of Kr on YB14 at $0.05 < \phi < 0.15$, but found that there was not a reasonable constant.

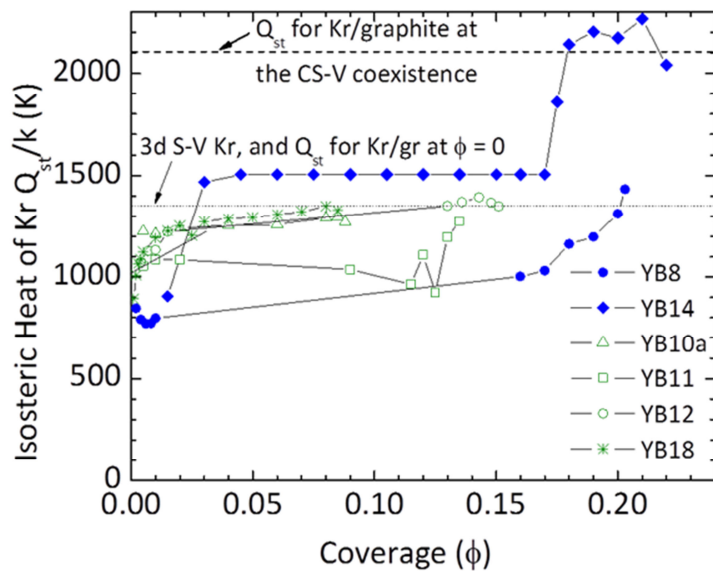


Figure 4.4 (a) - Isosteric heat of Kr calculated with the original pressure reading as described in text

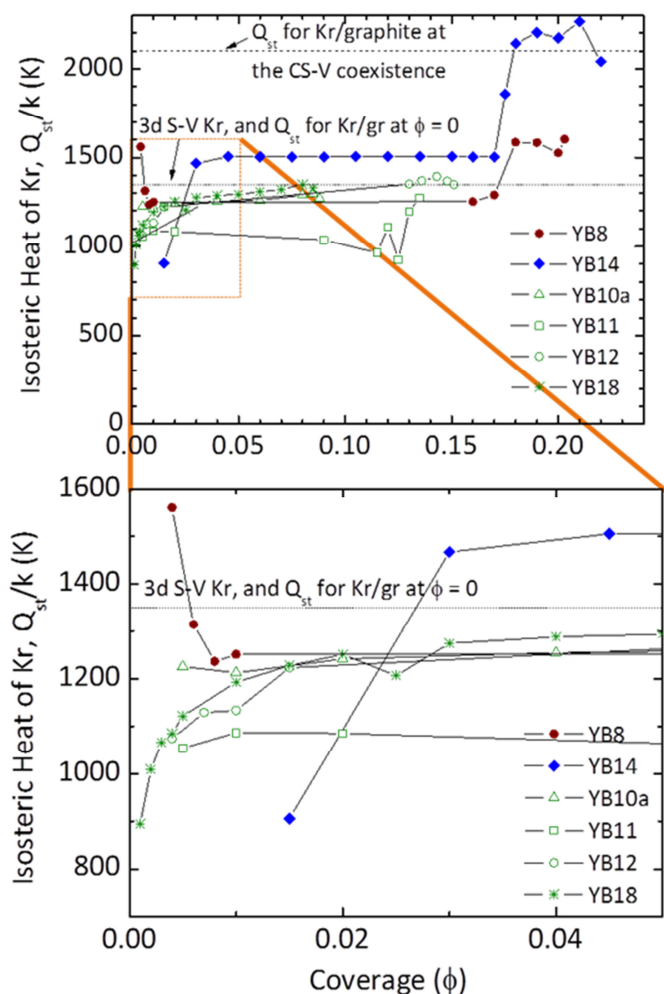


Figure 4.4 (b) – Isosteric heat of Kr calculated with the re-zeroed pressure reading as described in text

Figure 4.4 (c) – Enlargement of Figure 4.4 (b) in the low coverage region

In the figures, we indicate the latent heat of fusion of 3d Kr, the Q_{st} of Kr adsorbed on exfoliated graphite at $\phi = 0$, and the Q_{st} of Kr adsorbed on exfoliated graphite at the CS-V coexistence (from volumetric isotherms obtained by Thomy et al. (31) and Larher (32). Specht et al. published a review of the many phases found for Kr adsorbed on graphite (91). A summary of all measurements prior to 1996 is in Ref. (17). At zero coverage, the Q_{st} of Kr on all the nanotubes, maybe except device YB8, is considerably lower than on graphite. In the L-V coexistence $0.05 < \phi < 0.15$, the Q_{st} of Kr on all the nanotubes is significantly lower than the Q_{st} of Kr adsorbed on exfoliated graphite at the CS-V coexistence, while the Q_{st} of Kr at the S-L coexistence on nanotube YB14 is about the same with the Q_{st} of Kr on graphite at the CS-V coexistence.

We see in Fig. 4.4 (c), except for YB8 and YB10a, that $Q_{st} \approx 950 \text{ K} \pm 100 \text{ K}$ at very low coverage. Roughly speaking, the binding energy of Kr is about $950 \text{ K} - \frac{3}{2} \times 70 \text{ K} = 845 \text{ K}$, or about 35% lower than on graphite (90). In the “condensation” region, $0.02 < \phi < 0.15$, see Fig. 4.4 (b), the isosteric heat of Kr on YB14 is larger than for class 2 devices by about 250 K (YB10a, YB12, and YB18) and 400 K (YB11). This additional Q_{st} is due, likely, to the 2d L-V phase transition latent heat.

When comparing isosteric heat of Kr on different devices in Fig. 4.4 (a), (b), and (c), the YB14 data was calculated from isotherms at $T = 76 \text{ K}$ and 78 K since they are complete isotherms, measured from vacuum to 3-dimensional saturated pressure. They are below the 2D $T_c \sim 78 \text{ K}$, of Kr on YB14 and are closer to the temperatures of isotherms used to analyze other devices. In fact, there is some ambiguity in the calculation of isosteric heat of Kr on YB14. In Fig. 4.5, we show the Q_{st} of Kr on YB14 calculated from isotherms at different temperatures. There is a large variance of Q_{st} among different choices of isotherms, partially due above 78 K to the lack of a good correlation between ϕ and G .

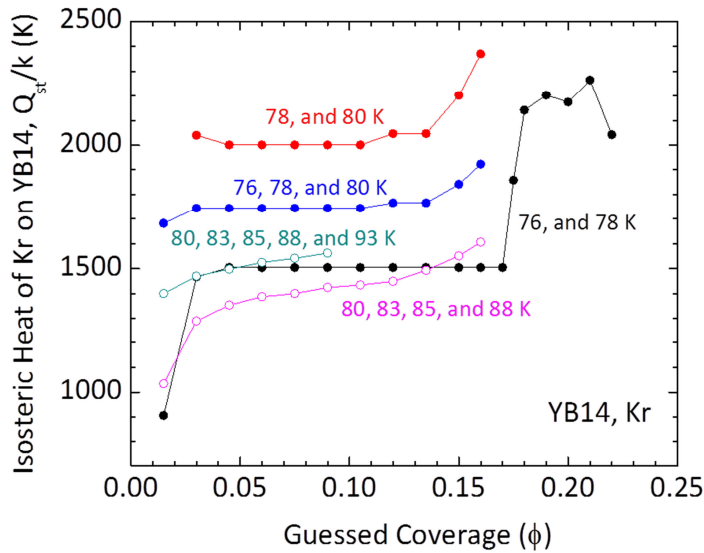


Figure 4.5 – Isosteric heat of Kr on YB14 calculated from isotherms of different temperatures – The isotherms at 80, 83, 85, 88, and 93 K are all above the L-V critical temperature ($\sim 78 \text{ K}$).

The isosteric heat of Kr on YB8 increased as the coverage decreased at the very low coverage, $\phi < 0.01$. Since YB8 behaved as a clean individual nanotube for the isosteric heat of Ar data, we suspect that the pressure reading happened not to be exactly correct at the low pressures when this device was measured with Kr, instead of consider device YB8 being two crossing nanotubes.

4.4 2D Latent Heat of Ar and Kr on YB14

From detailed and good data of the isotherms of class 1 devices, we are able to deduce the latent heat of the adsorbates. Here, the Ar isotherms on SWNT YB14 offer a good example.

Picking up the middle point of the large riser of each YB14 Ar isotherm, plotting the points in one diagram, letting the x-axis be $1/T$ and the y-axis be $\ln P$, the minus of the slope would be the isosteric heat, see Fig. 4.6.

In this device the slope changed at $T \sim 51$ K, between the 2D T_c , 54 K, and the 2D T_t , 48 K. For the temperature range from 47 K to 50 K, the slope magnitude is about 1440 K. For the temperature range from 51 K to 70 K, the slope magnitude is about 1040 K. The difference of the slopes, 400 K, is consistent with rough estimate of the 2d Ar latent heat, $3\varepsilon = 120 \text{ K} \times 3 = 360 \text{ K}$, where ε is the Lennard-Jones potential minimum for the interaction between two Ar atoms (92). The difference of the slopes is also reminiscent of the heat-capacity peak (peaks) of Ar on graphite, see Fig. 4.7 (25). The large peak in heat-capacity happened at $T \sim 50$ K, between the 2D T_c , 54 K, and 2D T_t , 48.5 K, of Ar on graphite.

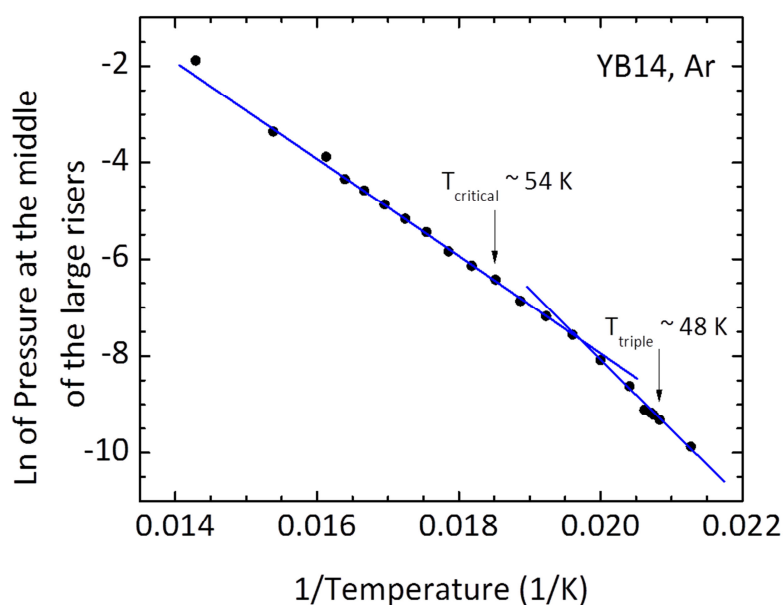


Figure 4.6 – Temperature versus pressure of the middle points of the large risers in the YB14, Ar isotherms – The $\ln(P)$ versus $1/T$ points fit two straight lines. The lines meet at $T \sim 51$ K.

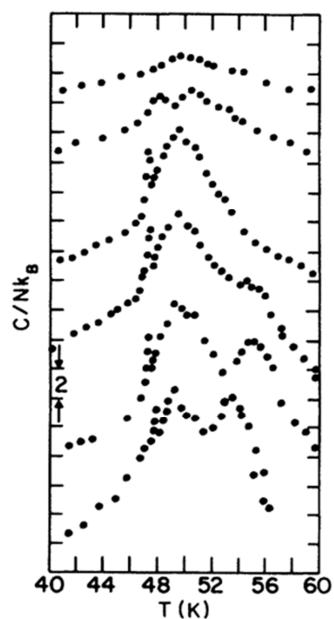


Figure 4.7 - Heat-capacity scans of Ar on graphite at coverages (from bottom to top) $n = 0.175, 0.572, 0.717, 0.872, 1.043$, and 1.068 – Adopted from Migone et al. (25)

In Fig. 4.8, we looked at the YB14 data in more detail, and plotted the isosteric heat of Ar on YB14 calculated with respect to isotherms at $47 \text{ K} \leq T \leq 49 \text{ K}$ and $54 \text{ K} < T < 70 \text{ K}$ separately. At $0.01 \leq \phi \leq 0.2$, for $47 \text{ K} \leq T \leq 49 \text{ K}$, Ar on YB14 had the L-V coexistence, and the Q_{st}/k was a constant, about 1440 K, while for $54 \text{ K} < T < 70 \text{ K}$, Ar on YB14 had the fluid state, and Q_{st}/k gradually increased as ϕ increased, but remained considerably lower, about 400 K, than Q_{st}/k for $47 \text{ K} \leq T \leq 49 \text{ K}$.

From data for $54 \text{ K} < T < 70 \text{ K}$, we see an increase in Q_{st} of Ar on YB14 at $\phi \sim 0.21$. Unfortunately, the isotherms are not clear enough to calculate the isosteric heat for ϕ higher than that. So for $\phi > 0.23$, we calculated Q_{st}/k of Ar on YB14 with respect to some other isotherms at $52 \text{ K} < T < 56 \text{ K}$, and it showed the 2D S-L, Ar latent heat.

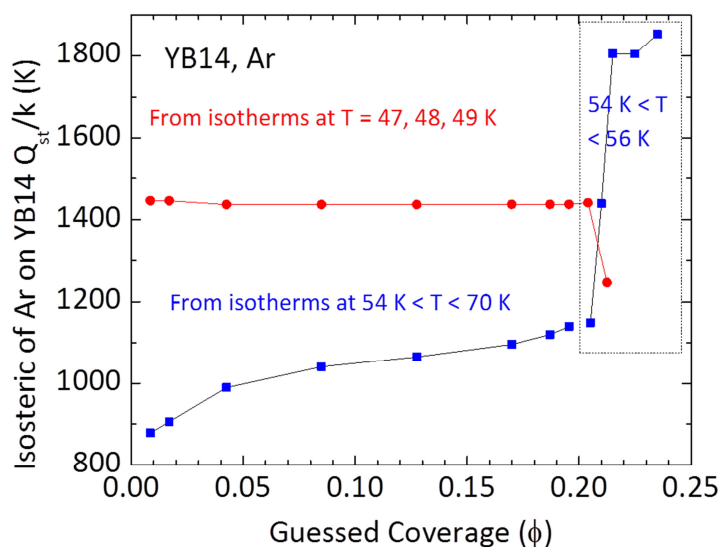


Figure 4.8 – The isosteric heat of Ar on YB14 calculated with respect to isotherms at $47 \text{ K} \leq T \leq 49 \text{ K}$ and approximate isosteric heat $54 \text{ K} < T < 70 \text{ K}$

In Fig. 4.9, we picked up the middle point of each YB14 Kr isotherm, plotting the points in one diagram, letting the x-axis being $1/T$ and y-axis be $\ln P$, the minus of the slope would be close to the isosteric heat like what we did for Ar on YB14.

However, in this figure, from $T = 80 \text{ K}$ to $T = 93 \text{ K}$, disregarding the point at $T = 95 \text{ K}$, the data shows an almost straight line, while from $T = 74 \text{ K}$ to $T = 80 \text{ K}$, the four points can only be joined by a curved line. The change in the slope is discontinuous at about $T = 80 \text{ K}$, a little bit above the $2D T_c$, $\sim 78 \text{ K}$, of Kr adsorbed on YB14. If we fit the points from $T = 80$ to 93 K with a straight line, the slope magnitude of the line at $80 \text{ K} \leq T \leq 93 \text{ K}$ will be about 1520 K . If we fit the two points at $T = 78$ and 80 K with another straight lines, the slope magnitude of the line will be about 2022 K . The difference of the slopes, 502 K , was consistent with rough estimate of the $2d$ Kr latent heat, $3\epsilon = 164 \text{ K} \times 3 = 492 \text{ K}$, where ϵ is the Lennard-Jones potential minimum for the interaction between two Kr atoms. But, we do not have a good reason why we should ignore the isotherm at $T = 76 \text{ K}$, and use the data at $T = 78 \text{ K}$ and 80 K to fit the lower temperature line.

If we fit the three points at $T = 76, 78$, and 80 K with a straight line, the slope will be 1753 K . The difference between this slope and 1520 K is 233 K , significantly lower than $3\epsilon = 492 \text{ K}$.

Another maybe acceptable choice is that, fitting points at $80 \text{ K} \leq T \leq 88 \text{ K}$ with a straight line, and fitting points at $76 \text{ K} \leq T \leq 80 \text{ K}$ with another straight line. The slope of the line at $80 \text{ K} \leq T \leq 88 \text{ K}$ is 1402 K , and the slope of the line at $76 \text{ K} \leq T \leq 80 \text{ K}$ is 1753 K . The difference is 351 K .

If we consider the straight line only fits the three points at $T = 80, 83,$ and 85 K, the slope will be 1220 K. Comparing the slopes of the line fits data at $80 \text{ K} \leq T \leq 85 \text{ K}$ and the line fits data at $76 \text{ K} \leq T \leq 80 \text{ K}$, the difference of the slopes, i.e. the latent heat based on this choice of data, is 533 K. It is more consistent with the theoretical estimated latent heat, $3\varepsilon = 492$ K, but again we do not have a good reason why we should neglect the isotherms at $T = 88$ K and 93 K.

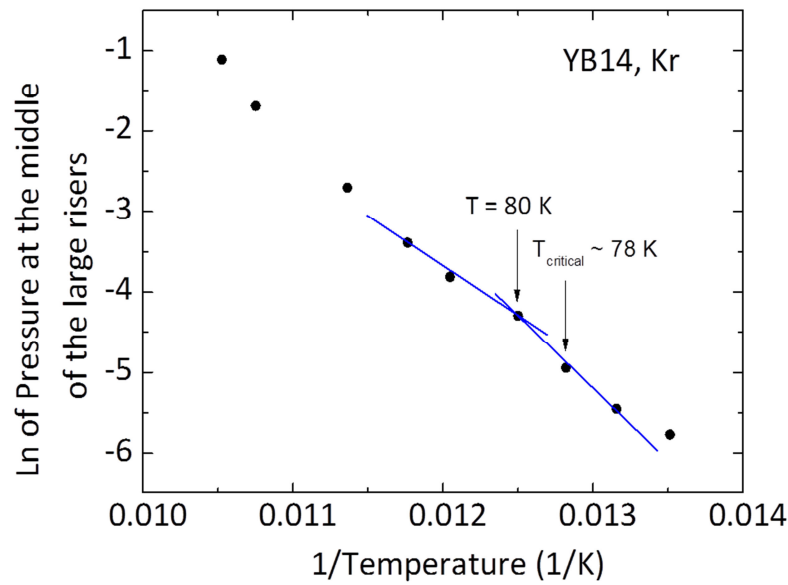


Figure 4.9 – Temperature versus pressure of the middle points of the large risers in the YB14, Kr isotherms described in text

5. Conclusion

In this Chapter, we give a summary of the results we obtained and discussed, and will mention what is going to be done or can be done for further research in the future.

5.1 Summary

We studied the effect of adsorbates of Ar and Kr on single-walled carbon nanotubes by measuring the adsorption and conductance isotherms of devices with the exposure to these noble gases. We discussed difference of SWNTs, diameters of the nanotubes, the phase transitions of the adsorbates, isosteric heat and binding energy of the adsorbates on the devices, and also the two-dimensional latent heat of Ar on a nanotube.

The background of physical adsorption, binding energy, and phases of noble gases on graphite were introduced in Chapter 1. We also described the properties of carbon nanotubes, and some previous work of the study of vibration resonance of carbon nanotubes and the study of adsorption effects on the conductance of devices. My work followed Z. Wang's PhD dissertation. Some of his results were shown, and were discussed and compared with mine.

In Chapter 2, we talked about the experimental procedure, including the device fabrication, the circuit and gas system setup, and how we measured the resonance frequency and conductance of the SWNTs to obtain the adsorption and conductance isotherms.

The results of measurements are shown in Chapter 3. There was a large riser in each isotherm. The pressures of the large risers depended on the temperatures of the isotherms, and also depended on the nanotubes and the adsorbates (Ar, Kr, etc.). On some of the SWNTs, the large risers were totally vertical at some low enough temperatures, indicating the co-existence of 2D vapor and 2D liquid states of the adsorbates on the nanotubes, and there were also small steps following the large risers, indicating the 2D liquid–solid phase transition.

Based on the isotherms, the SWNTs seemed like if they could be separated into two classes. We used the following four features to discuss the classes of the devices:

1. The pressures of the risers in the isotherms of the devices,
2. Whether the slope of the risers became vertical at low enough temperatures,
3. Whether there were clear, small steps following the large risers, indicating the 2D S-L phase transition,
4. The maximum overage that could be obtained on the SWNT at the saturated vapor pressure.

In Chapter 4, we calculated the radii of the SWNTs with respect to the coverage of the incommensurate solid state, and found that $R_0 \sim 1$ nm for YB3 (2 nm diameter) and $R_0 \sim 1.5$ nm (3 nm diameter) for YB8.

The 2D liquid-vapor critical and solid-liquid-vapor triple temperatures of the adsorbates on class1 devices were discussed. For Ar adsorbates on YB14, T_{triple} was about 48K, T_{critical} was about 53.8 K, and on YB8, T_{critical} was about 54 K. For Kr on YB8, T_{critical} was about 80 K, T_{triple} was about 68 K, and for Kr on YB14, T_{critical} was about 77.9 K, T_{triple} was about 73 K.

The 2D compressibility of Ar adsorbates on several devices was calculated at $T > T_{\text{critical}}$. The logarithm of the inverse compressibility versus logarithm of reduced temperature of YB14 (class1 device) was a straight line with slope being 7/4, see Fig. 4.1, as expected from the 2d Ising model. For YB11 (class2 device), when T_{critical} is assumed to be 54 K, the logarithm of the inverse compressibility converged to a constant, about -0.84, as the temperature decreased and approached 54 K. It suggests inhomogeneity on the surface of nanotube YB11.

The binding energy and isosteric heat of the gases on the SWNTs were studied, and were lower than what they are on graphite. The lower binding energy allowed us to measure the isotherms to lower temperatures as compared to graphite with the same limit of low pressure accuracy. The isosteric heats of Ar on the SWNTs were more consistent, and converged to about 800 ± 50 K as the coverage decreased to zero. For class 1 devices, the isosteric heat of Ar showed the 2D L-S transition latent heat, and likely also showed the 2D L-V phase transition. The isosteric heat of Kr on the SWNTs varied between devices.

By analyzing the middle point of each YB14 Ar isotherm, letting x-axis being $1/T$ and y-axis being $\ln P$, we found that the data looked like a straight line with the sloped changing at $T \sim 50$ K. The change of the slope was about 400 K, consistent with an estimated 2d Ar latent heat, $3\epsilon = 120 \text{ K} \times 3 = 360 \text{ K}$, where ϵ is the Lennard-Jones potential minimum for the interaction between 2 Ar atoms.

Measurements of isotherms on some devices with ^4He and Xe were made, but the data are limited. We measured Xe isotherms on device YB14, see Chapter 3. The results showed 2D co-existence phases. Binding energy of Xe on YB14 was also lower than on graphite. For ^4He , three adsorption isotherms were measured with device YB10, and the shift of conductance peak of YB14 was tracked with respect to the ^4He exposure. The binding of ^4He on the SWNTs was also lower than on graphite. If we can lower the temperature down to 1 or 2 K, it may be possible to measure the first-monolayer adsorption isotherms of both Helium isotopes on single-walled carbon nanotubes.

5.2 Future directions

There are lots of further research can be done on this topic. I only describe some of them here.

Binding Energy

Measuring the binding energy much more carefully, especially in the low coverage region, is meaningful. Although we did measurements of isotherms and calculated isosteric heat and binding, the detailed data are not enough, even for Ar. More carefully measured adsorption isotherms are required to determine the binding energy more accurately, to calculate the virial coefficients, and to find out the detail of how isosteric heat is related to the temperature.

Conductance Dependence on Coverage

It will be interesting to find out the relation between the coverage on a nanotube and its conductance. What we have seen is that the pressures of the large risers in the adsorption isotherms and conductance isotherms are consistent at the same temperatures with comparable source-drain bias voltage amplitudes. But, we do not know, in general, how the conductance depends on the adsorbates coverage. The change of conductance also was determined by the gate voltage the device was sitting on. For the

conductance isotherms the gate voltage was often chosen to be at the sharp side of, and close to the Dirac point. The effect of adsorbates on the conductance often looked like determined by the shift of the Dirac point. To have a complete picture, one may need to study the whole G - V_g dependence with respect to the exposure pressure, instead of looking at the conductance with only one fixed gate voltage.

Two Classes of SWNTs

More study of the two classes of SWNTs are needed. Based on the measurements, the devices were separated into two classes. It's not clear what makes the difference, and whether there are more classes. Detailed research on the nanotubes with theoretical analysis will be helpful to find out the mystery of the classes. We used 4 features to discuss the classes, but sometimes there is ambiguous in some features of some devices. It is also good to know how to clarify the classes better. A way to measure the diameter and chirality of each device, without destroying it, would be very important.

^4He and ^3He

Although we did not see a phase transition in the YB10 Helium isotherms and we only obtained conductance information of device YB14 with ^4He , the lower binding energy and the uniformity of the surface of at least some of single-walled carbon nanotubes may allow us to observe phase transitions of ^4He on SWNTs with isotherms at lower temperatures than on graphite with the same limit of the lowest pressure. If the temperature can be lowered to 2.5 or 3 K, we may be able to see a portion of the 2D phase diagram of the isotopes ^4He and ^3He adsorbed on the nanotube.

Polarized Molecules

For the experiments and research of adsorbates on SWNTs, we focused on Ar and Kr, but do not have much data with other gases. Both Ar and Kr are noble atoms. The structures of the atomic nucleus and the electronic cloud of them are all totally symmetric. It will be interesting to study gases with some different structures, for example polarized molecules. To find the effects of the polarization of the adsorbates, it will be helpful to compare a polarized molecule with a more symmetric one which has about the same mass. A good try will be comparing CO with N_2 . They have about the same mass, and the distributions of mass in the molecules are only slightly different. N_2 has a quadrupole moment, while CO has a dipole moment. By comparing them, we can see the difference between a permanent dipole and a permanent quadrupole moment. They are all studied on graphite.

Graphene

A single-walled carbon nanotube equals to a pristine curved sheet of graphene. Adsorbates on graphite had been well and widely studied. The adsorption on SWNTs is being studied now. Graphene has fascinating electronic properties (93). A sheet of pristine, not curved graphene under exposure to gases is in research (94) (95), and is requiring for more research. From the view of geometry, we expect that the binding energy of atoms on graphene is between that on graphite and on single-walled carbon nanotubes, see Fig. 5.1 (96).

We studied adsorption on a pristine exfoliated single-layer graphene on a substrate by conductance isotherms measurements using the cryocooler. The device was fabricated from graphene sheets by San-Feng Wu in Prof. Xiao-Dong Xu's lab without using any chemicals. We obtained reproducible Kr isotherms at $T = 80 \text{ K}$, $V_g = 0 \text{ V}$, see Fig. 5.2. There is a large riser in isotherms of this graphene device like

what we saw in the isotherms of SWNTs. The pressure where the riser happened in the graphene isotherms at $T = 80$ K is between the riser pressures of isotherms of graphite and SWNTs at the same temperature, as shown in Fig. 5.3. Unfortunately, the device stopped working after these isotherms were obtained. More measurements are needed for studying of adsorption on graphene. Are the 2D phase transitions of adsorbates on graphene, 2D critical and triple temperatures, and self-binding of the adsorbates on graphene similar to the ones on graphite, or do new phenomena appear? There are a lot of questions waiting for answers.

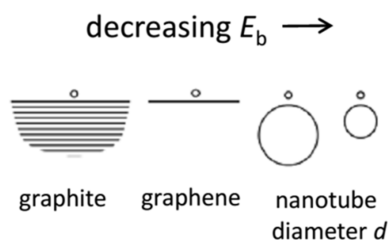


Figure 5.1 – View of geometry indicating the ordering of the binding energy of graphite, graphene, and single-walled carbon nanotubes.

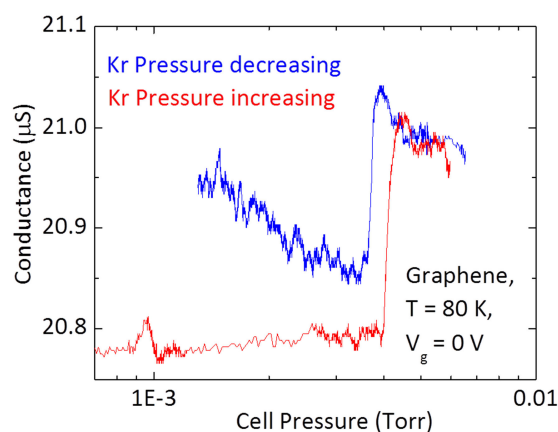


Figure 5.2 – Conductance isotherms on a piece of graphene with the pressure of Kr exposure increasing and decreasing at $T = 80$ K and $V_g = 0$ V

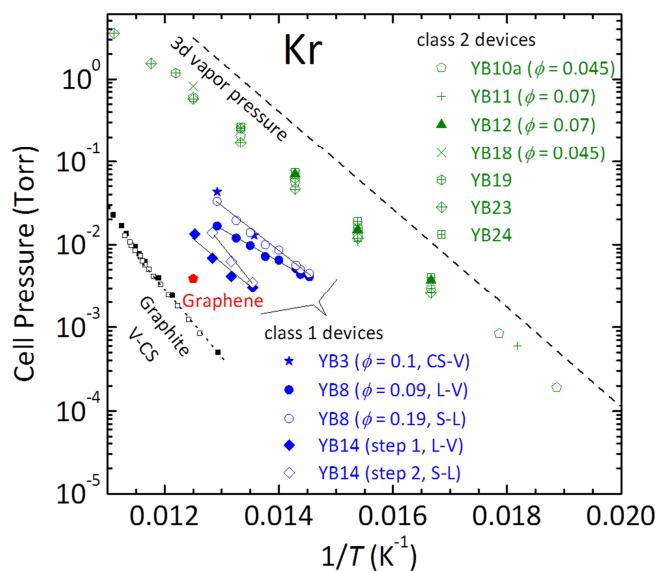


Figure 5.3 - Temperature-Pressure summary of the middle points of the large risers in the Kr isotherms of devices – The red mark presents the data of the piece of graphene at $T = 80$ K in Fig. 5.2, while the blue marks present data of devices YB3, YB8, and YB14, and green marks present data of other SWNTs, YB10a, YB11, YB12, YB18, YB19, YB23, and YB24. The data of Kr on graphite are plotted with black marks.

Appendix

A1. Class 1 devices

YB3, YB8, and YB14 looked like belong to one class, while other SWNTs we measured looked like belong to another.

YB8

YB8 was measured in the liquid nitrogen cryostat by Z. Wang.

Ar

All the Ar isotherms are shown in Fig. A1.1. In each isotherm there was one smooth, large riser. The maximum coverage ϕ is about 0.25. In three of the isotherms, it's followed by a smaller, almost vertical riser in the range $0.2 < \phi < 0.24$. The small riser became more pronounced as T decreases.

For crystalline Ar the density of its (111) planes is $\phi \sim 0.22$ at 50K [Pollack], comparable to the maximum density observed in Low Energy Electron Diffraction (LEED) experiments with Ar/graphite $\phi \sim 0.21$ at 42K [Shaw1979]. Thus, this small riser corresponds to the crossing of the 2d fluid-solid coexistence region.

The lowest temperature measured was 68.2 K. The slope of large risers increased as the temperature decreasing. Extrapolating the inverse slope to lower temperature until the inverse slope is zero, we estimate that the isotherms will become vertical when the temperature decreased to about 54 K. It is natural to interpret that the 2D T_{critical} is about 54 K, the smooth, large risers present the fluid phase of Ar adsorbates, which will become vertical showing the vapor-liquid V-L transition at $T < T_{\text{critical}}$. The smaller risers are the fluid-solid (F-S) transitions.

The maximum coverage that can be attained, which is limited by the Ar 3d saturated vapor pressure of $P_{\text{vapor}} = 10$ Torr that is reached in the 70.2 K isotherm, is about 0.25. This is quite close to the estimated $\phi_{\text{Ar,max}}$ for a 1-nm radius nanotube.

Once P_{vapor} is reached it is impossible to build a second layer.

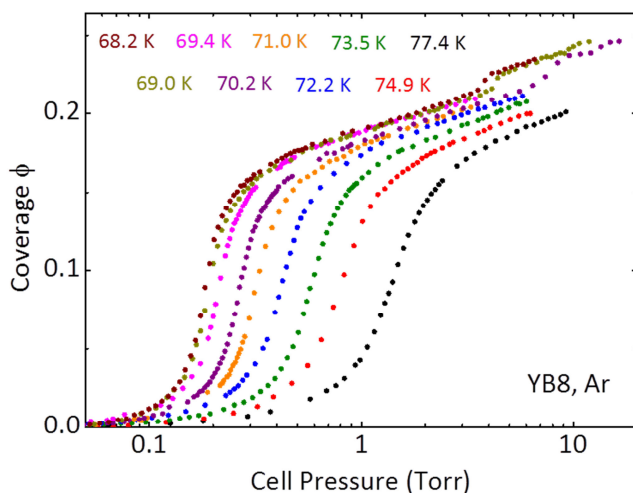


Figure A1.1 - Ar isotherms on device YB8 – All isotherms were measured at T larger than L-V critical temperature. Three isotherms (68.2, 69.0 K, and 70.2 K) showed the solid formation step at $\phi \sim 0.22$. (80)

Kr

All the Kr isotherms are shown in Fig. A1.2. In each isotherm there was one large riser, too sharp to be resolved with the pressure intervals used, followed by a smaller, smoother riser in the range $0.18 < \phi < 0.19$. It is natural to interpret the large riser as the Kr vapor-liquid (V-L) transition since the size of the large jump increased as T was lowered, and the smaller one as a liquid-solid (L-S) transition (where we do not know whether the solid is commensurate or not).

The maximum coverage that can be attained, which was limited by the Kr 3d saturated vapor pressure of $P_{\text{vapor}} = 1.75$ Torr that was reached in two of the 77.4 K isotherms, is about 0.22. This was quite close to the estimated $\phi_{\text{Kr,max}}$ for a 1-nm radius nanotube, and was larger than the one of adsorbed atoms to carbon atoms on flat graphite where $\phi_{\text{max}} \sim 0.186$. This was again consistent with the larger diameter of the monolayer than the nanotube.

Once P_{vapor} was reached it was impossible to build a second layer. There was a small shift in ϕ in the third isotherm at 77.4 K which reflected the uncertainties in reproducing an isotherm after several cycles.

For YB8 we could not go above 77.4 K. Its L-V critical point T_c would be close to 80 K as estimated from the decrease in the magnitude of the larger vertical step (the coexistence region).

The S-V and L-V lines converged to what should be the S-L-V triple point, $T_t \sim 68$ K, slightly below the lowest measured temperature.

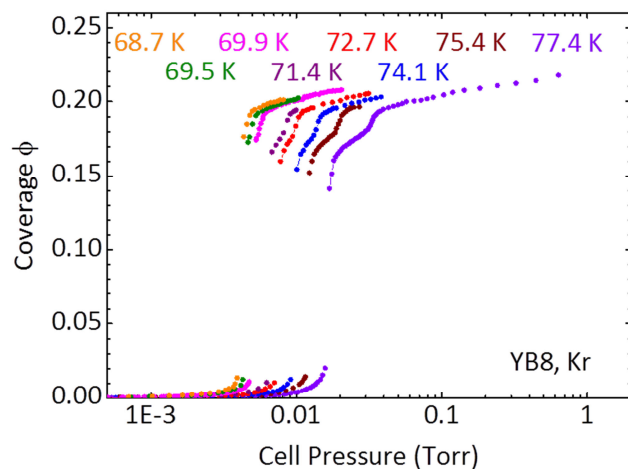


Figure A1.2 – Kr isotherms on YB8 – Note the disappearance of the long vertical step as T went up, and the converge of the long and small vertical steps as T went down. (80)

YB3

YB3 was also measured in the liquid nitrogen cryostat by Z. Wang. After the measurement with Ar, only two Kr isotherms were measured before the device stop functioning. These isotherms were reported in Ref (79).

Ar

The Ar coverage isotherms of YB3, see Fig. 1.3, behaved similarly to the Ar isotherms of device YB8. For the measured temperature region, 66.1 K to 77.4 K, the isotherms show large, smooth risers, following by a small step at $\phi \sim 0.24$ if the resonance can be seen there. The maximum coverage $\phi \sim 0.26$ is slightly larger than on device YB8.

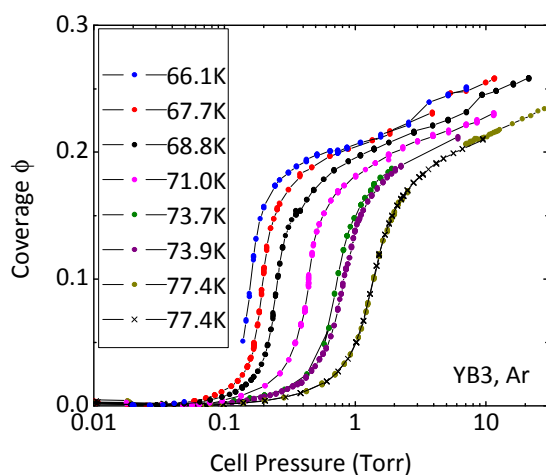


Figure A1.3 – Ar adsorption isotherms on device YB3 – Data was taken by Z. Wang. (79) (80)

Kr

The Kr coverage isotherms, see Fig. A1.4, show a large vertical transition and a series of small step. The pressures of the large risers in YB3 Kr isotherms were slightly higher than YB8 isotherms at the same temperature. One of the small steps at $\phi \sim 0.2$ indicated liquid – incommensurate solid transition (like what YB8 Kr isotherms do), but the 77.4 K isotherm also show a small feature at $\phi \sim 0.17$ ($\sim 1/6$) which could indicate a commensurate solid state. The maximum coverage of the 77.4 K isotherm is $\phi_{\max} \sim 0.23$ at $P \sim 1.75$ Torr, the saturated vapor pressure at this temperature.

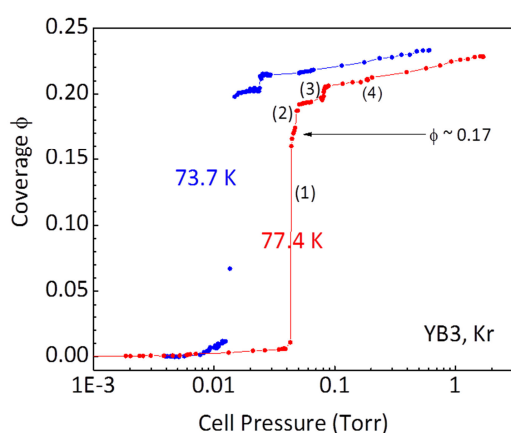


Figure A1.4 – Kr isotherms on device YB3 – Only two isotherms were obtained. Several (almost) constant P steps were observed. Step (1) seemed to end at $\phi \sim 0.17$, very close to the $\phi = \frac{1}{6} = 0.167$, that would correspond to a commensurate solid as observed on Kr/ graphite. Data was taken by Z. Wang. (79) (80)

YB14

YB14 was measured using the cryocooler. The data on YB14 were obtained purely from conductance measurements. There is no clear resonance found in the mixing current.

Ar

There is a change in the G-Vg graph due to the Ar adsorbates. We fixed the gate voltage at which the G-Vg has the sharpest slope to measure the conductance isotherms, see Figs. A1.5 (a) and (b).

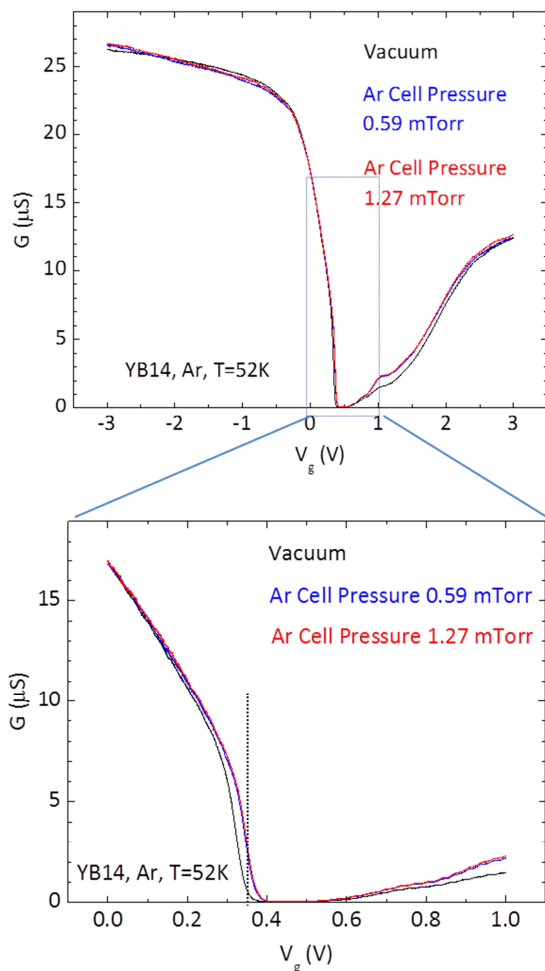


Figure A1.5 (a) - The conductance versus gate voltage of device YB14 at two constant Ar pressures, 0.59 mTorr and 1.27 mTorr, at $T = 52$ K

Figure A1.5 (b) - Enlarged region of Figure A1.5 (a)

The complete set of Ar isotherms is shown in Fig. A1.6. In each Ar isotherm there was one large riser. The pressures of the YB14 Ar isotherms are almost one order lower than isotherms of YB3 and YB8 at the same temperatures. For isotherms at temperatures lower than about 54 K, the large risers were too sharp to be resolved with the pressure intervals used, and there were spikes occurring at the bottom of the large risers.

The large risers were followed by a smaller, smoother riser when the temperatures were between 48 K and 54 K, see Fig. A1.7(a). When the temperatures were lower than 48 K, there was no small riser following, but the large risers ended with spikes at the top. At temperatures higher than 54 K, the large risers were smooth, followed by the smaller riser. There were no spikes shown in the isotherms.

It is natural to interpret the large riser as the Ar vapor-liquid (V-L) transition for $48\text{ K} < T < 54\text{ K}$, as the Ar vapor-liquid (V-S) transition for $T < 48\text{ K}$, and the smaller one as a liquid-solid (L-S) transition, see the description in chapter 3 and discussion in chapter 4.

In chapter 4, section 2, we observed that the 2D triple temperature, T_{triple} , was about 48 K , and the 2D critical temperature, T_{critical} , was about 53.8 K .

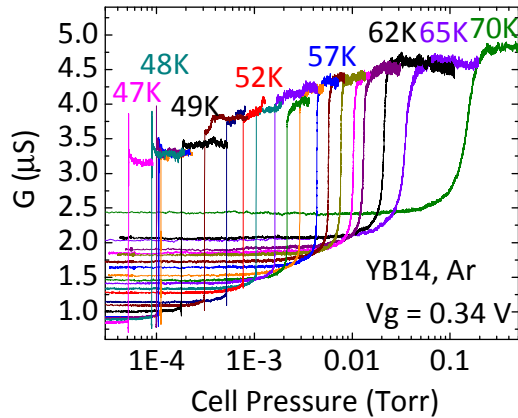


Figure A1.6 - The complete set of Ar isotherms measured on device YB14 – The complete set of temperatures, from the lowest to the highest, was in Kelvin, 47, 48, 48.163, 48.256, 48.455, 49, 50, 52, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 65, 70.

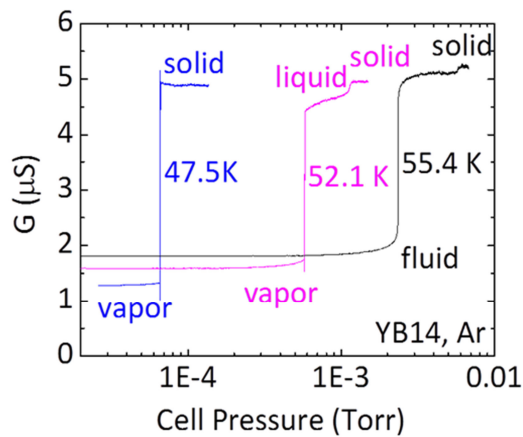


Figure A1.7(a) – Three Ar isotherms measured on SWNT YB14 at $T = 47.5\text{ K}$ ($T < T_{\text{triple}}$), $T = 52.1\text{ K}$ ($T_{\text{triple}} < T < T_{\text{critical}}$), and $T = 55.5\text{ K}$ ($T > T_{\text{critical}}$) – Note that the small step above the large riser corresponded to the 2d L-S (or F-S) transition when $T > T_{\text{triple}}$.

Fixing the gate voltage and let $T = 51 \text{ K}$ ($T_{\text{triple}} < T < T_{\text{critical}}$), we let in and pumped out Ar very slowly around the pressure range of the 2d L-V transition on YB14, see Fig. A1.7 (b). We saw fluctuations in conductance when the Ar vapor adsorbates became liquid on the surface of the SWNT.

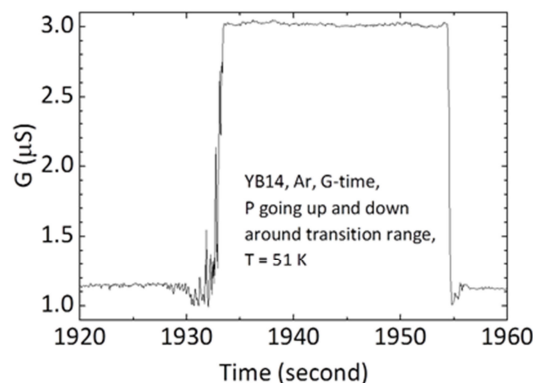


Figure A1.7 (b) – conductance of YB14 versus time as Ar pressure going up and down around the 2d L-V transition range at $T = 51 \text{ K}$ – Fluctuations were seen in the conductance when the vapor Ar adsorbates on YB14 became liquid.

Kr

The variation of the conductance versus gate voltage at $T = 74 \text{ K}$ with two different pressures of Kr is shown in Fig. A1.8. The full set of Kr isotherms is shown in Fig. A1.9. In each Kr isotherm there was one large riser. The pressures of the YB14 Kr isotherms are a little less than one order lower than isotherms of YB3 and YB8 at the same temperatures. For isotherms at temperatures lower than about 80 K , the large risers looked like vertical. The large risers were followed by a smaller, smoother riser.

We interpret the large riser as the Kr vapor-liquid (V-L) transition, and the smaller one as a liquid-solid (L-S) transition (where we do not know whether the solid was commensurate or not) in the 74 K , 76 K , and 78 K isotherms. These isotherms were discussed in chapter 4 where we deduced that the $2d T_{\text{critical}} \sim 77.9 \text{ K}$, and $2d T_{\text{triple}} \sim 73 \text{ K}$.

We are not sure what the little features and the tilting larger risers which followed the small steps were.

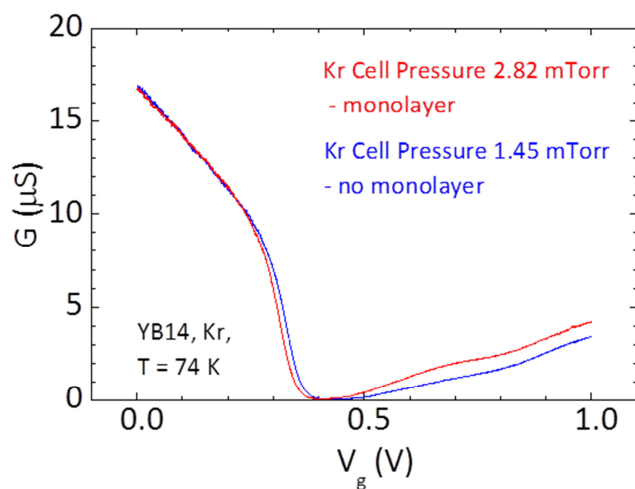


Figure A1.8 - Variation of the conductance with respect to the gate voltage of YB14 nanotube at 74 K with two different Kr pressures.

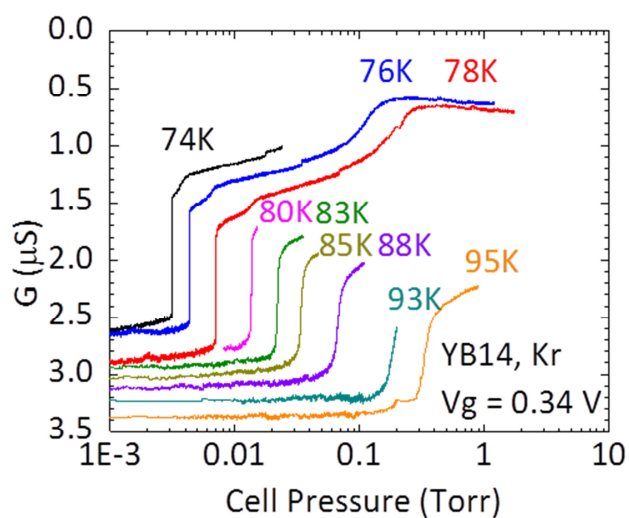


Figure A1.9 – The full set of Kr isotherms on device YB14.

He

The isotherm measurements were done in the temperature range $4.1 \text{ K} < T < 8.5 \text{ K}$. At these low temperatures, there were Coulomb blockade peaks in G as a function of V_g which lead to complications in the conductance isotherms.

We measured G - V_g while ^4He was pumped out of the cell at $T = 7.5 \text{ K}$. The diagram shifted as the ^4He pressure decreased, see Fig. A1.10. To obtain an isotherm, we employed a method slightly different to

that described in the experimental section: rather than fixing V_g , we tracked the value of V_g associated with a given Coulomb blockade peak as a function of P . The drift of the blockade peaks first moved towards higher V_g , but near the completion of the monolayer they reversed direction. The isotherms are shown in Fig. A1.11. These isotherms were not G vs. P , but $V_g^{(\text{maximum})}$ vs. P .

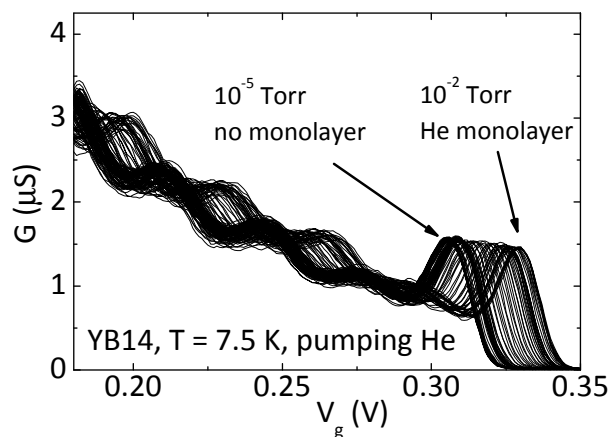


Figure A1.10 – Coulomb blockade oscillation of the conductance of the YB14 device and their dependence on adsorbed ^4He at $T = 7.5$ K

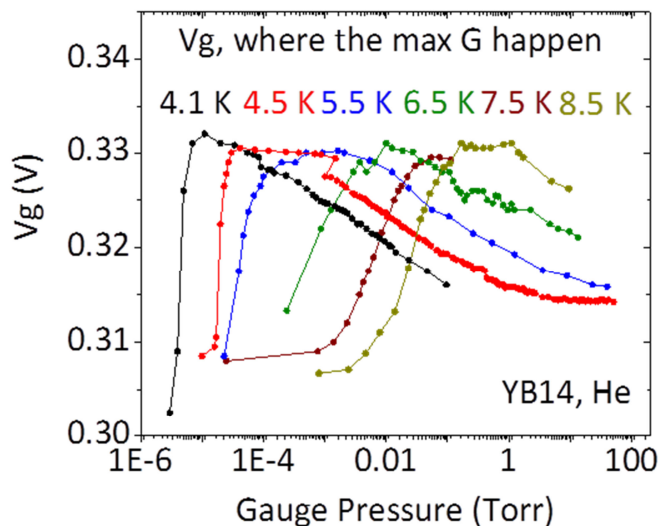


Figure A1.11 – ^4He $V_g^{(\text{maximum})}$ isotherms of device YB14

Xe

We measured 8 isotherms over the temperature range where solid, liquid, and vapor phases had been observed for Xe adsorbed on graphite, see Fig. A1.12. For the Xe conductance isotherms of YB14 we only

see the large risers, either sharp (indicating vapor-liquid V-L transitions) or smooth (fluid, for $T > T_{\text{critical}}$), but we do not find clear features for the liquid-solid L-S transitions.

$T_{\text{critical}} \sim 115$ K, was obtained by extrapolating the inverse slopes of the 120 K, 130 K, and 140 K isotherms. We can not tell what T_{triple} is since we can not find the L-S transitions.

The data of Xe was not as noise-free as the data for Ar, Kr, and He. We are not sure whether it was due to the difference of gas, or whether it was that the device was not as good as before after all the measurements with Ar, Kr, and He.

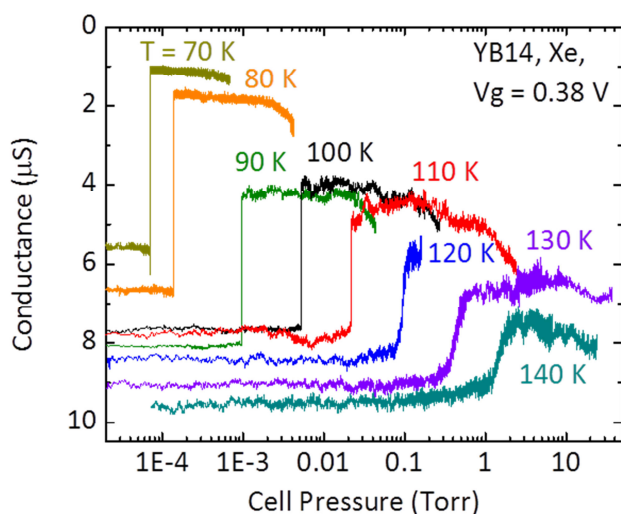


Figure A1.12 – The complete set of Xe conductance isotherms obtained with device YB14.

Fixing the temperature and gate voltage, we also measured the current I_{dc} versus the direct source-drain bias V_{dc} , with and without Xe in the cell, see Fig. A1.13. When V_{dc} was not too high, $I_{\text{dc}}-V_{\text{dc}}$ with enough Xe in the cell was definitely different than the one obtained in vacuum. It showed the effect of adsorbates on conductance. When V_{dc} was high enough, $I_{\text{dc}}-V_{\text{dc}}$ with enough Xe in the cell joined the $I_{\text{dc}}-V_{\text{dc}}$ in vacuum. It is interpreted as the power, $I_{\text{dc}}-V_{\text{dc}}$, heating the nanotube, so that the Xe adsorbate was evaporated.

Careful study of $I_{\text{dc}}-V_{\text{dc}}$ graphs for different pressures of gas in the cell and different temperatures may let us correlate the power to the temperature difference given by heating.

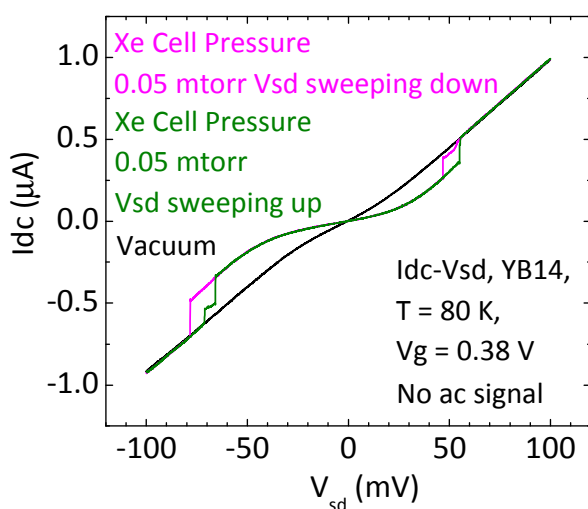


Figure A1.13 – Observing adsorption and desorption of Xe on YB14 via the source drain bias varying

A2. Class 2 devices

Class 2 devices: Large risers of the isotherms showed higher pressures than for Class 1 devices at equal temperatures. A full monolayer occurred at considerable lower surface density. The transitions did not appear to be vertical at low temperatures. No clear feature showed the solid phase in the isotherms.

All the following devices fell into class 2. They were all measured using the cryocooler.

YB10 (ϕ): ^4He , YB10a (ϕ and G) : Ar, Kr, YB11 (ϕ) : Ar, Kr, YB12 (ϕ and G) : Kr, YB16 (G) : Ar, YB18 (ϕ and G) : Ar, Kr, YB19 (G) : Ar, Kr, YB23 (ϕ and G) : Ar, Kr, N₂, YB24 (ϕ and G) : Ar, Kr

SWNT YB10 was only measured with ^4He , I will show the data at the end of all the devices.

YB10a

Experiments were done with Ar and Kr. Data of adsorption and conductance were obtained.

Ar

The Ar adsorption isotherms of YB10a are shown in Fig. A2.1. There was one large riser in each isotherm. The pressures at the risers were about 1 order of magnitude higher than YB3 and YB8 for the same temperature, and more than one order of magnitude higher than YB14. The slopes were constant and were not infinite at the lowest temperatures. There was no small step as the fluid-solid phase transition. ϕ_{max} is about 0.11.

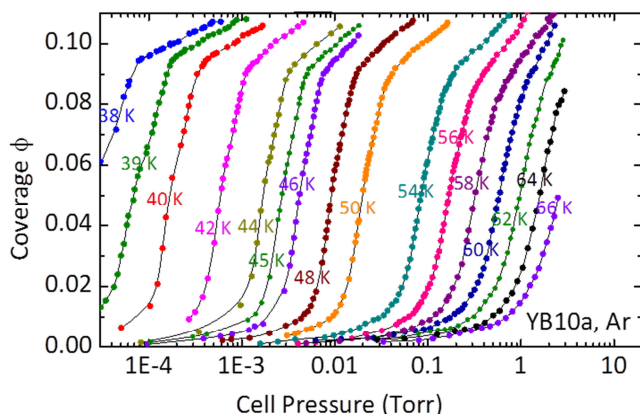


Figure A2.1 - The complete set of Ar adsorption isotherms measured on device YB10a – The complete set of temperatures, from the lowest to highest, is in Kelvin, 38, 39, 40, 42, 44, 45, 46, 48, 50, 54, 56, 58, 60, 62, 64, 66.

In the G-V_g diagram of YB10a, Fig. A2.2, we see that the conductance is modified by the Ar adsorbates.

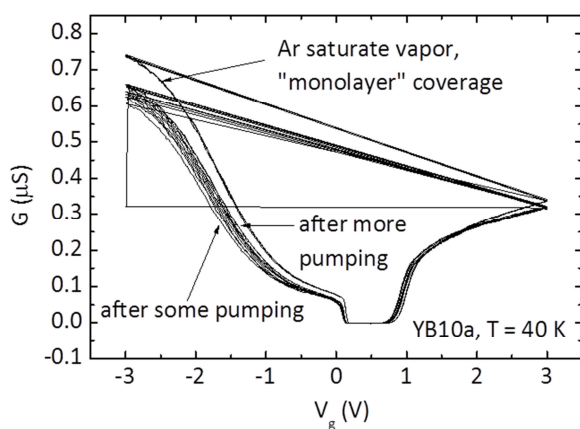


Figure A2.2 – Conductance versus gate voltage for YB10a with continuous pumping from the maximum possible Ar coverage at T = 40 K

Fixing V_g at -2 V, T at 44 K, we measured the Ar conductance isotherms for YB10a. As the Ar pressure increased, the conductance decreased first and then increased and then decreased a little bit again, see Fig. A2.3. The pressure where the large riser happens in the conductance isotherm is consistent with the coverage isotherm. And the pressure where the conductance had the minimum is about the pressure where the coverage started to increase quickly.

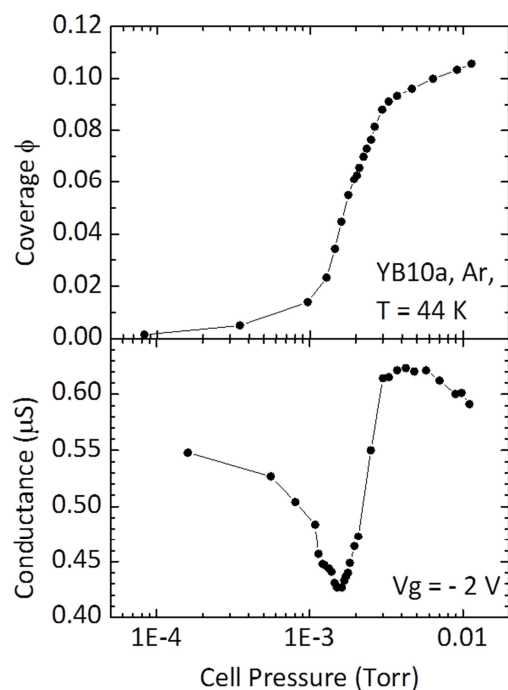


Figure A2.3 – Adsorption (ϕ) and conductance (G) Ar isotherms of YB10a at $T = 44$ K and $V_g = -2$ V

Kr

The Kr coverage isotherms of YB10a are shown in Fig. A2.4. There was one large riser in each isotherm. The pressures at the risers were about 1 order of magnitude higher than YB3 and YB8 for the same temperatures, and more than one order of magnitude higher than YB14. The slopes were constant and were not infinite at the lowest temperatures. There was no small step as the fluid-solid phase transition. $\phi_{\max}$ was about 0.09.

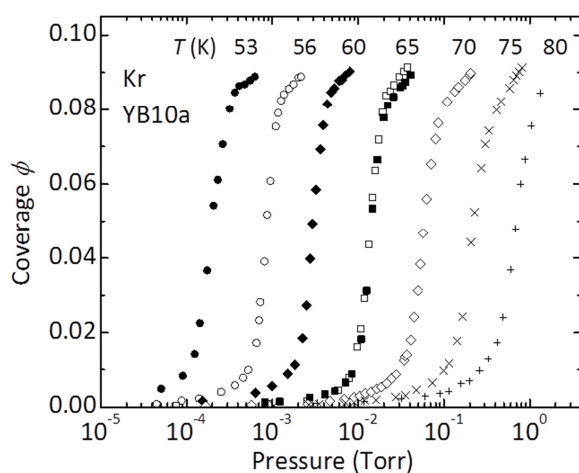


Figure A2.4 - The complete set of Kr adsorption isotherms measured on device YB10a – The complete set of temperatures, from the lowest to highest, is in Kelvin, 53, 56, 60, 65, 70, 75, 80.

YB11

Most of the measurements were with Ar. But there were only 3 Kr adsorption isotherms.

Ar

The Ar coverage isotherms of YB10a are shown in Fig. A2.5. There was one large riser in each isotherm. The pressures at the large risers were slightly lower than YB10a. The slopes increased more and more slowly as the temperature decreased and were not infinite at the lowest temperatures. There seemed to be a sign of a small step at $0.13 < \phi < 0.15$ in the isotherms of temperature lower than about 52 K, but they were not as significant as what we see in the isotherms of YB3, YB8 and YB14. $\phi_{\max}$ was about 0.16.

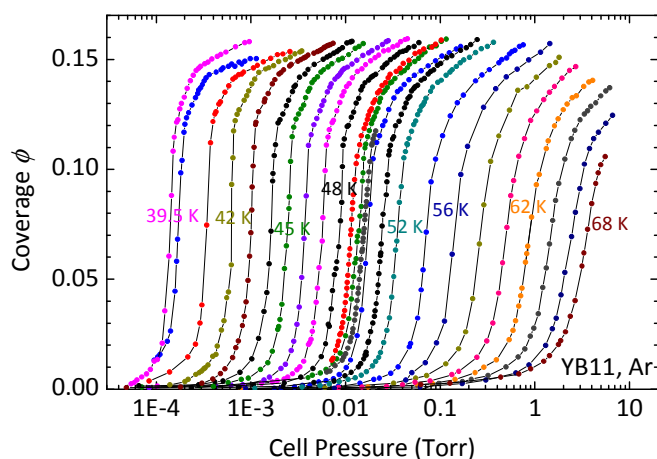


Figure A2.5 – The complete set of Ar adsorption isotherms on device YB11 – The complete set of Ar adsorption isotherms measured on device YB11 – The complete set of temperatures, from the lowest to highest, is in Kelvin, 39.5, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 49.4, 49.8, 50, 51, 52, 54, 56, 58, 60, 62, 64, 66, 68.

For YB11, the conductance was also modified by the Ar adsorbates. Zooming in the region near the Dirac point as shown in Fig. A2.6 (a) and (b), the G-Vg diagram was shifted by the adsorbates in this region. Around the Dirac point, it was shifted to the left first and then turned back to the right. The shift was clear and consistent. For $V_g \sim -0.5$ V as Ar was adsorbed the conductance decreased first, and then increased, see Fig. A2.6 (c). The change was not as clear as in the Dirac point region.

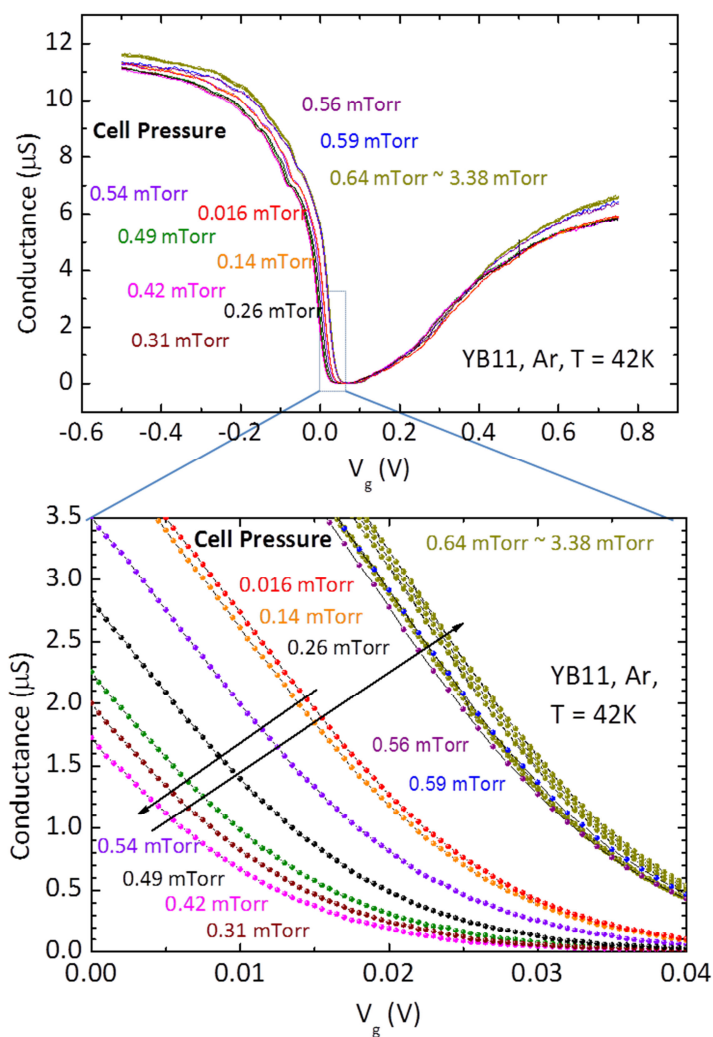


Figure A2.6 – Conductance of YB11 affected by Ar adsorption at $T = 42$ K
(a) The region $-0.6 \text{ V} < V_g < 0.8 \text{ V}$

(b) Enlargement of Fig. A2.6 (a) in the region near Dirac point

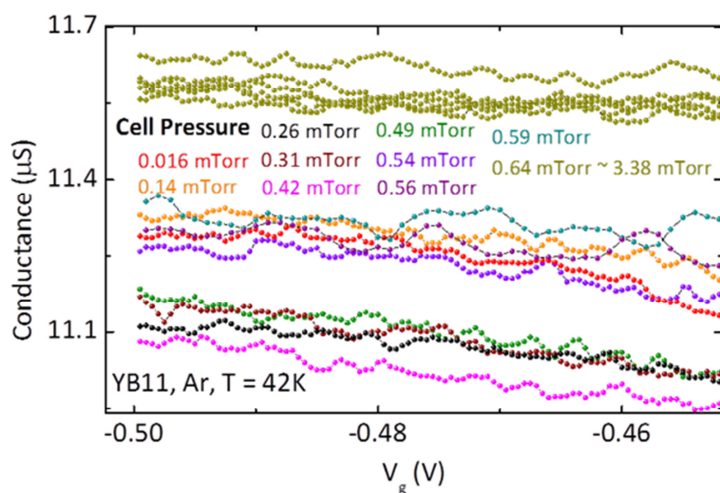


Figure A2.6 (c) – Conductance shifts with Ar adsorption for YB11 over a small region of V_g where G was almost constant

At $T = 52$ K, around the Dirac region, as the Ar adsorbates increased, the G - V_g graph shifted to the left side first, and then to the right side, and finally shifted back to the left a little bit as the Ar pressure reached saturation, see Fig. A2.7.

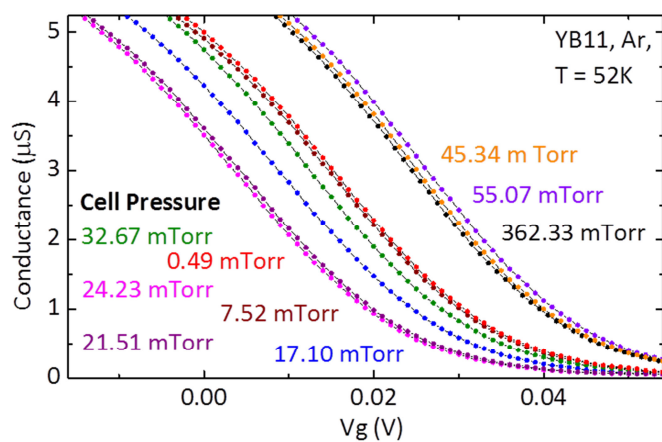


Figure A2.7 - Conductance of YB11 affected by Ar adsorption at $T = 52$ K for the region near the Dirac point

The adsorption and conductance isotherms measured at $V_g = 0.02$ V, $T = 42$ K, 47 K, and 52 K are shown in Fig. A2.8. The conductance isotherms show that as the Ar pressure increased, the conductance decreased first, and then increased (a large riser), finally it decreased a little bit again.

The pressures at which the large risers occurred in the conductance isotherms are consistent with the pressures where the large risers happen in the coverage isotherms for the same temperature. The pressures where the conductance has the minimum are about the pressure where the coverage starts to increase quickly.

Like YB10 (a), the pressure where the large riser happens in the conductance isotherm of YB11 is consistent with the coverage isotherm. And the pressure where the conductance had the minimum is about the pressure where the coverage started to increase quickly.

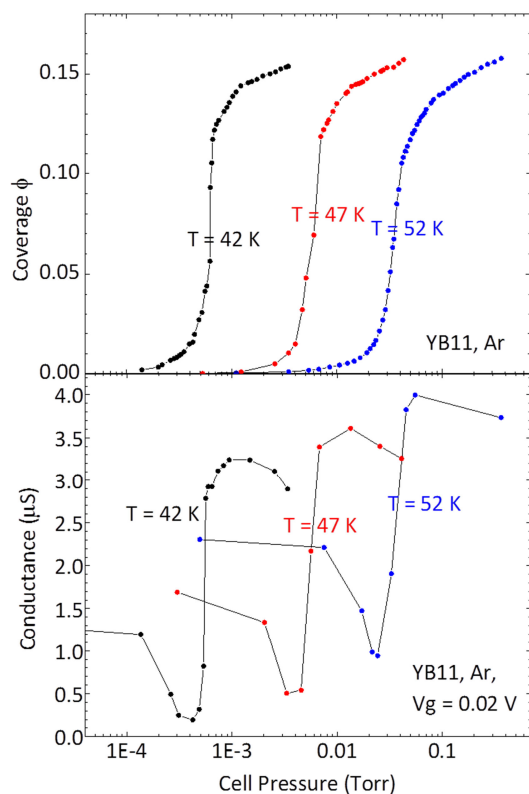


Figure A2.8 – Adsorption and conductance Ar isotherms of device YB11 at three temperatures – The conductance isotherms were measured with $V_g = 0.02$ V, near the Dirac point as shown in Fig. A2.6 (b) and A2.7

Kr

Only three coverage isotherms were measured on YB11, at 60, 65 and 70 K, before the device failed. None of these devices attained the expected coverage of a full monolayer when the 3d Kr vapor

pressure was reached. $\phi_{\max} \sim 0.14$. As the Kr pressure increased, the conductance of YB11 decreased first and then increased.

The pressures of the large risers of the coverage isotherms were also consistent with the pressures of the risers of the conductance isotherms at the same temperatures. The pressures where the conductance had the minimum were about the pressure where the coverage started to increase quickly, see Fig. A2.9.

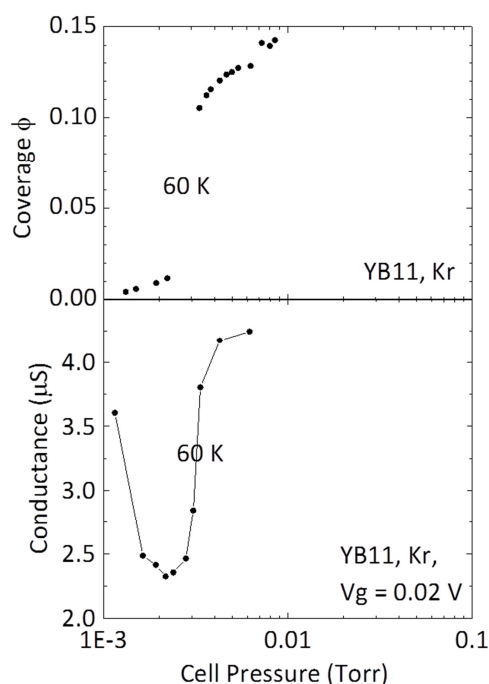


Figure A2.9 - Adsorption and conductance Ar isotherms of device YB11 at $T = 60$ K – The conductance isotherms was measured with $V_g = 0.02$ V.

YB12

YB12 was measured only with Kr. But we started to measure the adsorption and conductance isotherms at the exactly same pressure.

Kr

The Kr adsorption and conductance isotherms of YB12 are shown in Fig. A2.10. The pressures at the large risers in the isotherms for YB12 were an order of magnitude higher than for YB3, a little more than one order of magnitude higher than YB8 at the same temperatures, and also maybe slightly higher than YB10a and YB11. The maximum coverage ϕ was about $0.15 \sim 0.16$, well below the value for YB8.

Isotherms of the conductance of YB12 at 60 K, 65 K and 70 K, were measured at the same time as the adsorption isotherms. Relatively sharp risers in the conductance always coincide with those in ϕ , and can

therefore be used as an alternative means to detect the phase transitions. However, the variation in conductance between runs and the lack of a theory to connect conductance changes with temperature and adsorbate density make the conductance isotherms, for now, useful only for detecting sudden density changes due to phase transitions.

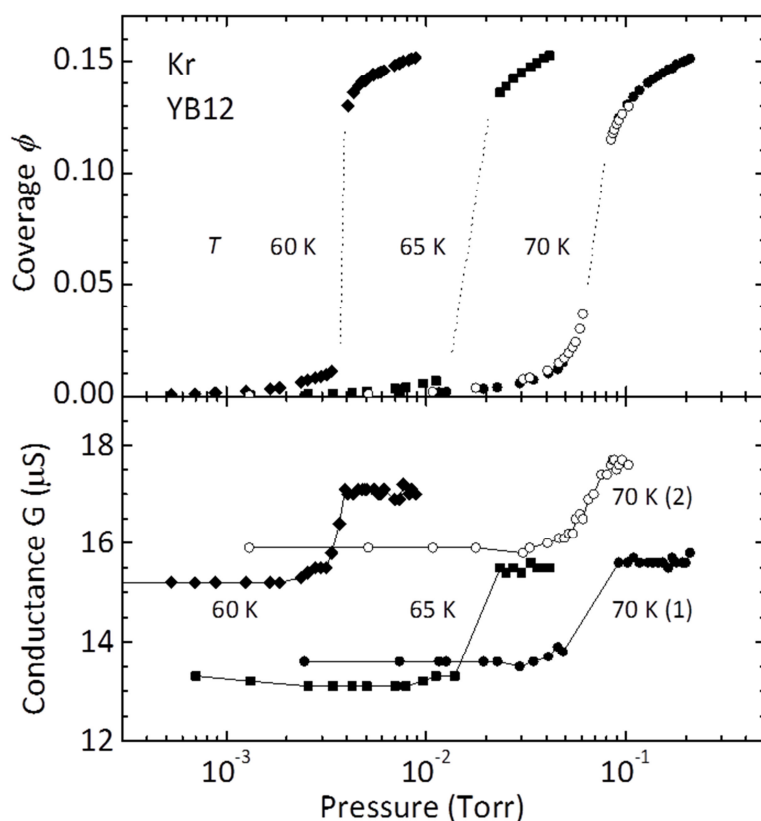


Figure A2.10 – Adsorption and conductance isotherms of device YB12 measured with Kr at $T = 60, 65$, and 70 K – We measured the ϕ and G isotherms twice at 70 K . Comparing them, we found that the adsorption isotherm remained the same while the conductance was shifted.

The Kr conductance isotherms of YB12 were about monotonic, while what for YB10a and YB11 were not. The slope of the large risers in the isotherms seemed to increase as the temperature decreased. Although, we did not see a totally vertical large riser at $T = 60\text{ K}$, the lowest temperature measured with this device. We did not find clear small step indicating S-L transition of Kr adsorbates in those YB12 Kr isotherms.

YB16

YB16 was only measured with Ar. No resonance was found in the mixing current. We measured the conductance.

Ar

The conductance of YB16 was small. At room temperature, the G - V_g diagram looked like a medium gap SWNT (between small gap and big gap), see Fig. A2.11 (a). After cooling down, the conductance was smaller than at room temperature, and the G - V_g looked like a big gap device, see Fig. A2.11 (b).

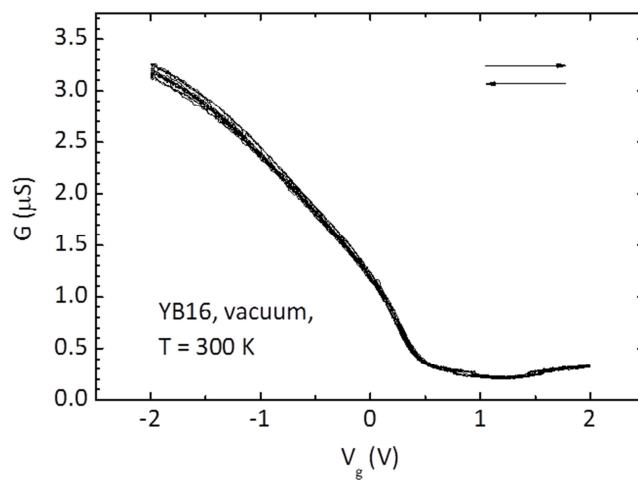


Figure A2.11 (a) – Conductance versus gate voltage of device YB16 in vacuum at T = 300 K

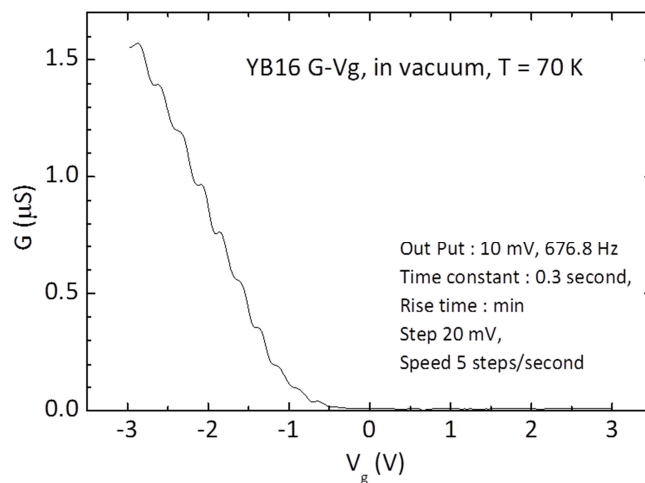


Figure A2.11 (b) - Conductance versus gate voltage of device YB16 in vacuum at T = 70 K

We measured the continuous conductance isotherms with Ar at $V_g = -1.8$ V, see Fig. A2.12 (a), (b). At first, there was a wire loosely touching the grounding, so that there was a huge noise in the signal detected. We used a very slow scan speed and a large time constant to deal with the noise. It helped. Although there was still noise in the signal, we saw a clear, large risers indicating phase transition in each conductance isotherms.

The pressures of the large risers indicate that this device was belong to class 2, but they were a little bit lower than the pressures of other class 2 devices. The slope of the large risers increased as the temperature of the isotherms decreased. Because of noise in the signal and pressure reading, we are not sure whether the slope was vertical or not at $T = 42$ K, the lowest temperature where we have a YB16 isotherm. We saw something like spikes at the top of the large risers in the isotherms at $T = 42$ K and 45 K. This kind of feature was not found with other class 2 devices.

The increasing of slope of the large risers can give an estimated 2D critical point of Ar on this device. But unlike the class 1 devices, we did not see promising features for liquid-solid transitions, and could not determine the 2D triple point.

After getting rid of the loosing wire, the noise problem was solved. The signal became very clean and clear. Unfortunately, the device died very soon after the noise problem solved. We did not have much data for this device.

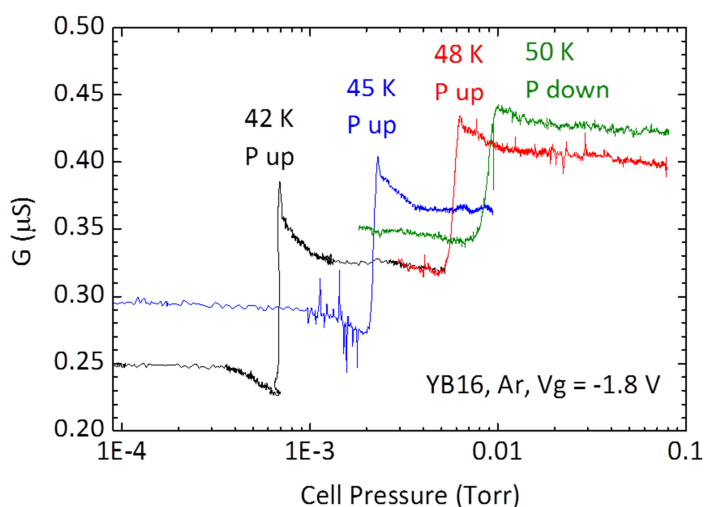


Figure A2.12 (a) – A set of conductance isotherms of device YB16 with Ar at $V_g = -1.8$ V – In the 50 K isotherm, Ar pressure was decreasing. In other three isotherms, Ar pressure was increasing.

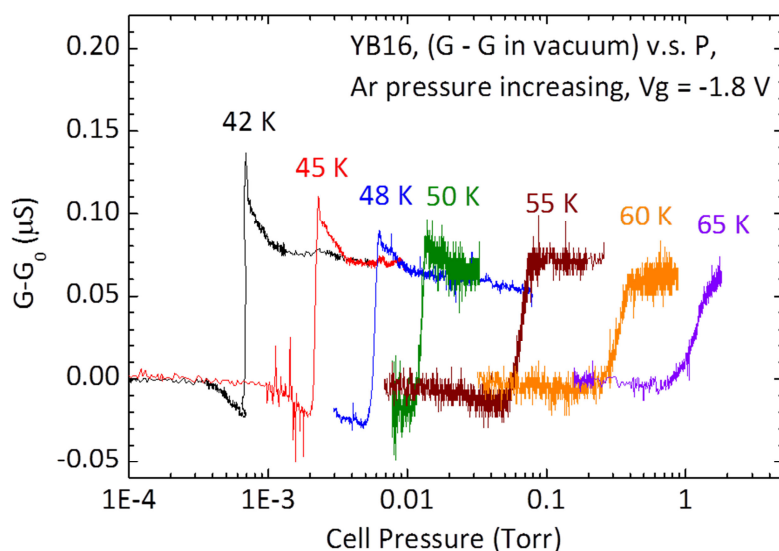


Figure A2.12 (b) - A set of conductance isotherms of device YB16 with Ar at $V_g = -1.8$ V - Ar pressure was increasing in all the isotherms.

YB18

YB18 was measured with Ar and Kr. We measured both the adsorption and conductance isotherms.

Ar

The adsorption and conductance Ar isotherms of YB18 are shown in Fig. A2.13. In each coverage isotherm, the large riser was smooth, the $\phi_{\max}$ was about 0.1, and there was no clear feature following the large riser. The pressure where the riser happened was slightly higher than the pressure of YB10a and YB11 at the same temperature. The slopes of the risers were always finite, and looked like constant even if the temperature reached 40 K. As the Ar pressure increased, the conductance decreased first and then increased (a large riser), finally decreased a little bit again, like how it behaved for YB10a and YB11.

The pressure of the large risers of the conductance isotherms were consistent with the pressure of the risers of the adsorption isotherms at the same temperatures. The pressures where the conductance had the minimum were about the pressure where the coverage started to increase quickly.

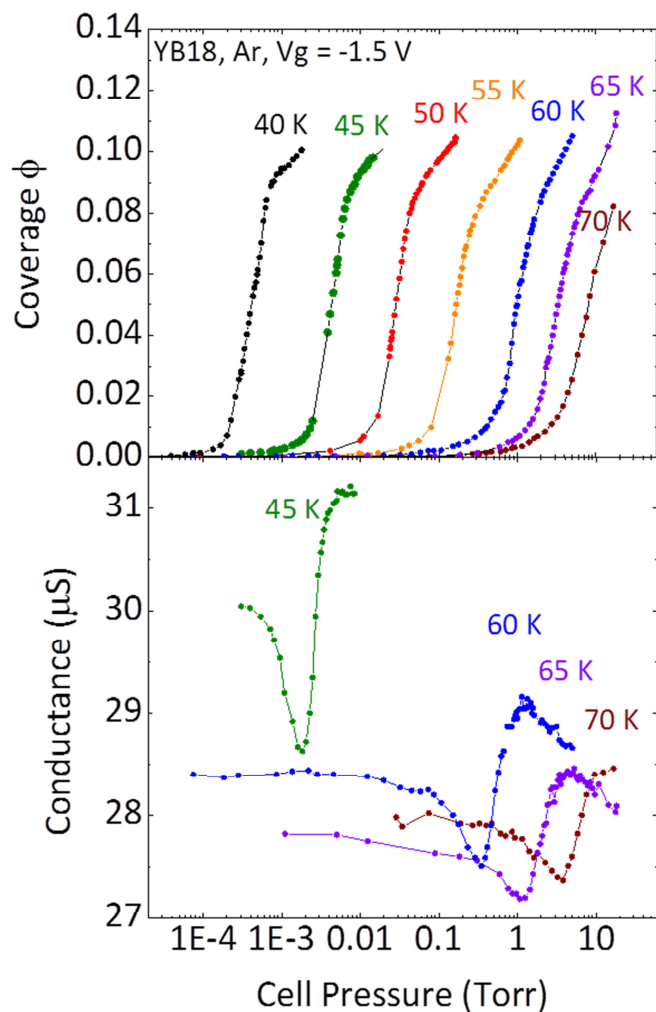


Figure A2.13 – Adsorption and conductance isotherms of SWNT YB18 measured with Ar, $V_g = -1.5$ V

$G-V_g$ of YB18 was measured with different Ar pressures, See Fig. A2.14 (a). Like YB11, around the Dirac region, as the Ar adsorbates increased, the $G-V_g$ graph shifted to the left side first, and then to the right side, and finally shifted back to the left a little bit as the Ar pressure reached saturation, see Fig. A2.14 (b). For $V_g \sim -1.4$ V as Ar was adsorbed the conductance decreased first, and then increased, see Fig. A2.14 (c).

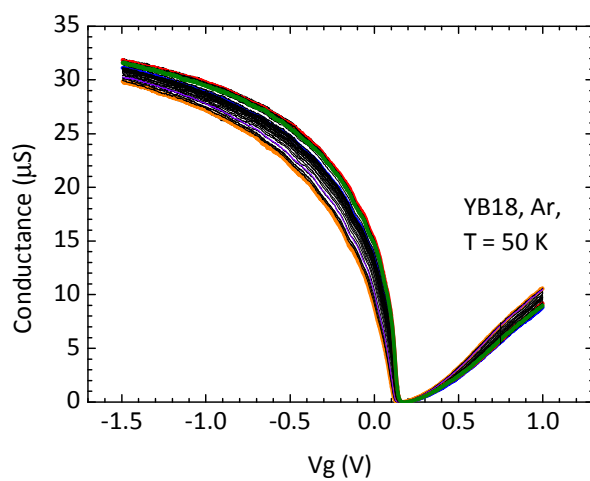


Figure A2.14 (a) – Conductance versus gate voltage of SWNT YB18 with different pressures of Ar, at T = 50 K

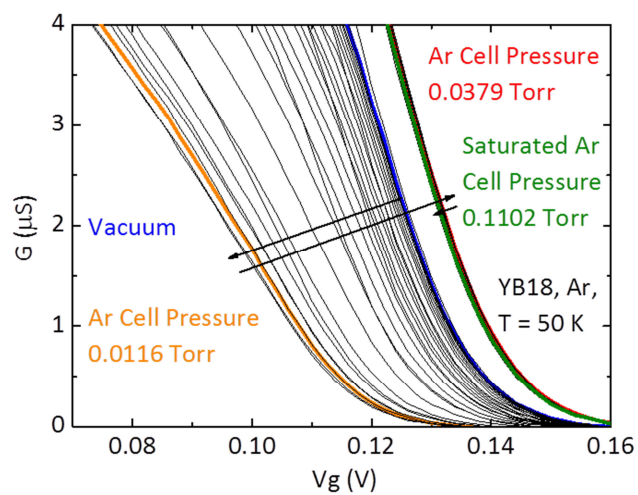


Figure A2.14 (b) - Enlargement of Figure A2.14 (a) around the Dirac Point

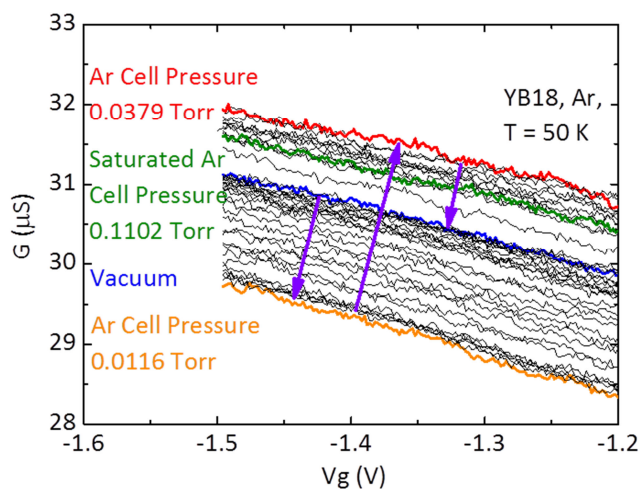


Figure A2.14 (c) - Enlargement of Figure A2.14 (a) around $V_g = -1.4$ V

Kr

The adsorption and conductance Kr isotherms of YB18 are shown in Fig. A2.15. The large risers of the Kr coverage isotherms were smooth. $\phi_{\max}$ was about 0.09. There was no clear feature following the large riser. The pressures of the risers of YB18 Kr isotherms were close to the pressures of YB10a at the same temperature. The slopes of the risers were always finite, even if the temperature was as low as 60 K.

Fixing V_g slightly left to the Dirac point, the Kr conductance isotherms behaved like the Ar conductance isotherms. As the Kr pressure increased, the conductance decreased first and then increased (a large riser), and finally decreased a little bit again, like how the conductance behaved for YB10a and YB11, but not YB12. The pressure of the large risers of the coverage isotherms was consistent with the pressure of the risers of the conductance isotherms at the same temperatures. The pressures where the conductance had the minimum were about the pressure where the coverage started to increase quickly.

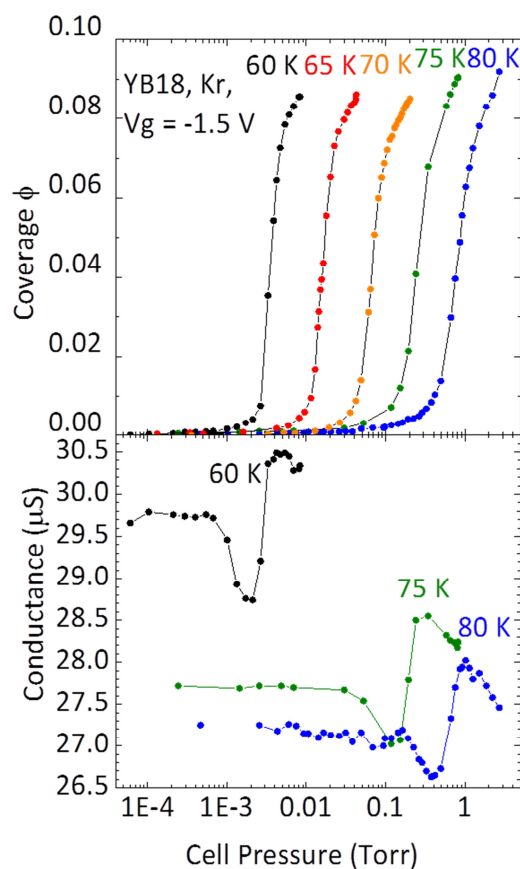


Figure A2.15 – Adsorption and conductance isotherms of SWNT YB18 measured with Kr, $V_g = -1.5$ V

$G-V_g$ of YB18 was measured with different Kr pressures, see Fig. A2.16 (a). Like YB18 measured with Ar, around the Dirac region, as the Kr adsorbates increased, the $G-V_g$ graph shifted to the left side first, and then to the right side, and finally shifted back to the left a little bit as the Ar pressure reached saturation, see Fig. A2.16 (b).

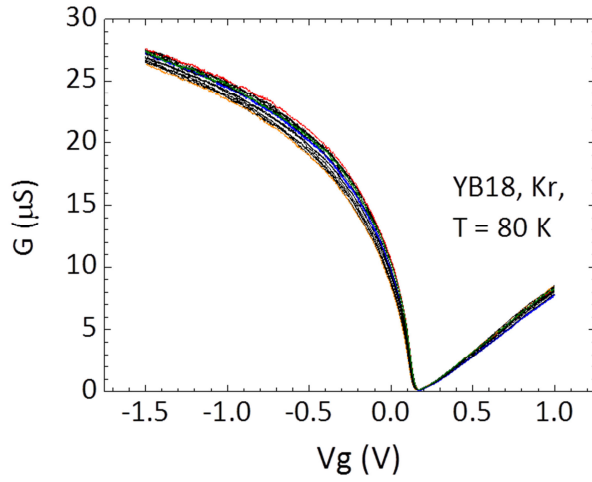


Figure A2.16 (a) - Conductance versus gate voltage of SWNT YB18 with different pressures of Kr, at T = 80 K

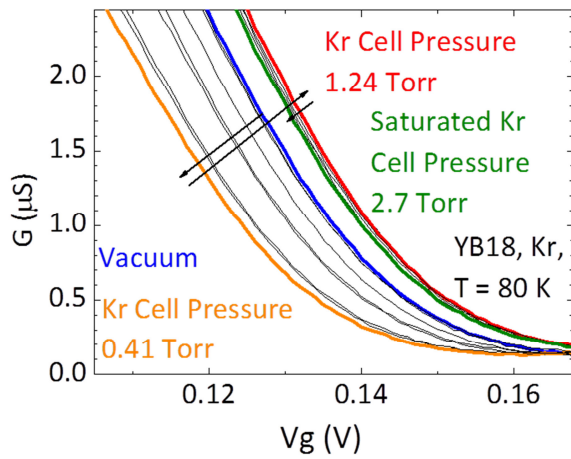


Figure A2.16 (b) - Enlargement of Figure A2.15 (a) around the Dirac Point

YB19

Device YB19 was measured with Ar and Kr. No resonance was found in the mixing current. Only conductance data was obtained.

Ar

Conductance versus gate voltage of YB19 was affected by Ar adsorbates, see Fig. A2.17 (a). Like YB11 and YB18, around the Dirac region, as the Ar adsorbates increased, the G - V_g graph shifted to the left side first, and then to the right side, and finally shifted back to the left a little bit as the Ar pressure reached saturation, see Fig. A2.17 (b).

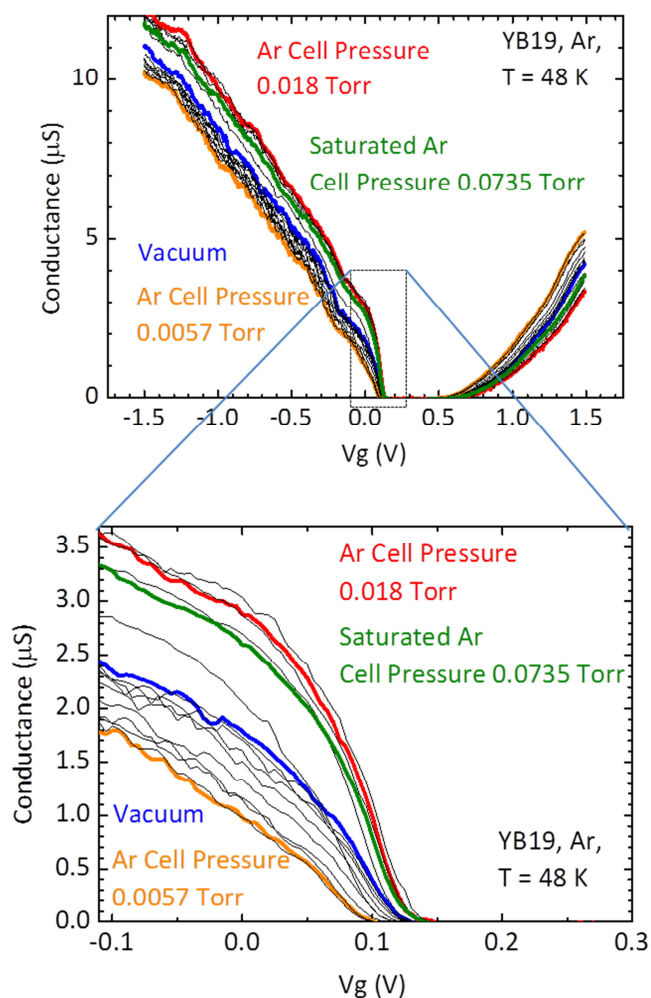


Figure A2.17 (a) - Conductance versus gate voltage of SWNT YB19 with different pressures of Ar, at $T = 48\text{ K}$

Figure A2.17 (b) - Enlargement of Figure A2.17 (a) around the Dirac Point

We measured the conductance Ar isotherms of YB19 at $V_g = 0$, see Fig. A2.18. Like YB10a, YB11, and YB18, as the Ar pressure increased, the conductance of YB11 decreased first and then increased (a large riser), and finally decreased a little bit. The pressures of the large risers were more closer to the pressures of YB18, and slightly higher than YB10a, YB11, and YB16 for isotherms at the same temperatures.

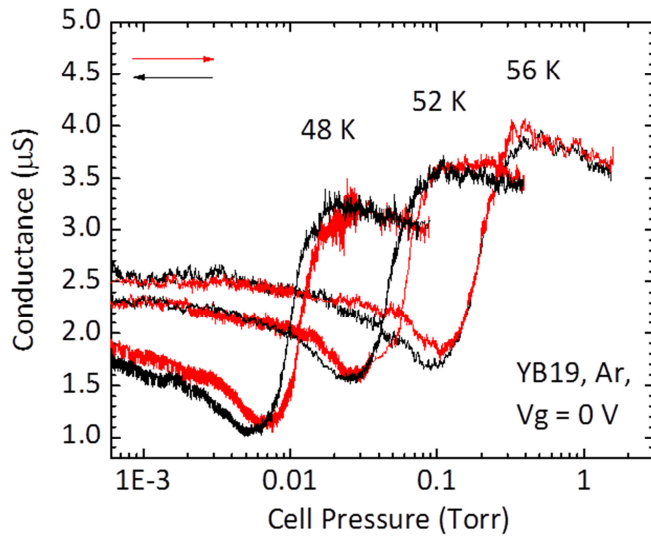


Figure A2.18 - Conductance isotherms of SWNT YB19 measured with Ar, $V_g = 0$ V

Kr

The G - V_g of YB19 with different pressures of Kr is shown in Figure A2.19 (a), (b). Conductance versus gate voltage of YB19 was affected by Kr adsorbates, see Fig. A2.19 (a). Like with Ar adsorbates, around the Dirac region, as the Kr adsorbates increased, the G - V_g graph shifted to the left side first, and then to the right side, and finally shifted back to the left a little bit as the Ar pressure reached saturation, see Fig. A2.19 (b). Coulomb Blockades were seen at V_g higher than the Dirac point. We did not see the Blockades when measured the device with Ar. Maybe the device was degraded with time.

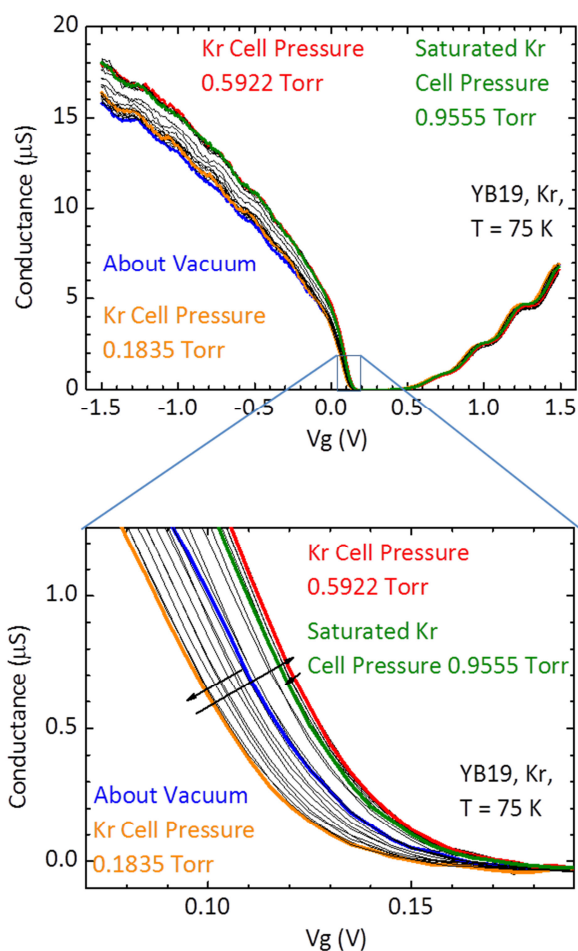


Figure A2.19 (a) - Conductance versus gate voltage of SWNT YB19 with different pressures of Kr, at $T = 75$ K

Figure A2.19 (b) - Enlargement of Figure A2.19 (a) around the Dirac Point

Conductance isotherms of device YB19 with Kr are shown in Fig. A2.20. With $V_g = 0$ V, as the Kr pressure increased the conductance slowly decreased first, and then increased quickly (a large riser), and finally decreased slightly again. The pressures of the large risers in YB19 Kr isotherms were close to the pressures of the large risers in YB18 Kr isotherms at the same temperatures.

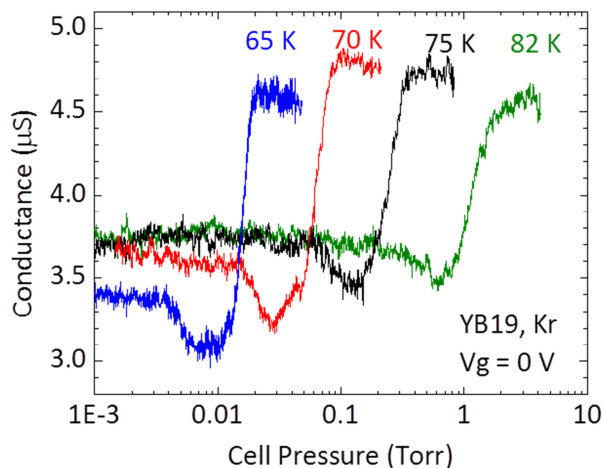


Figure A2.20 - Conductance isotherms of SWNT YB19 measured with Kr, $V_g = 0$ V

YB23

Device YB23 was measured with Ar and Kr. For Ar measurements, we obtained good adsorption isotherms, but not conductance ones. For Kr measurements, we obtained good conductance isotherms.

Ar

The Ar adsorption isotherms of YB23 are shown in Fig. A2.21. There was a large riser in each isotherm like other devices, but there was something different. There was a small step in low coverage part ($\phi \sim 0.02$) in at least 4 of the Ar adsorption isotherms of YB23.

The pressures of the large risers of YB23 Ar isotherms were slightly higher than the pressures of the large risers of YB10a and YB11, and more close to YB18 and YB19 for the same temperatures.

Conductance versus gate voltage of YB23 in vacuum and with saturated Ar exposure at $T = 50$ K was plotted in Fig. A2.22.

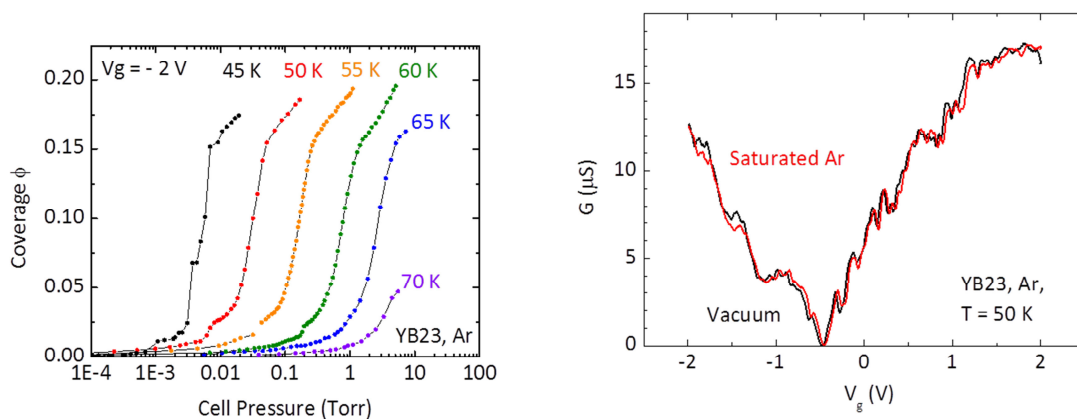


Figure A2.21 - Adsorption isotherms of SWNT YB23 measured with Ar, $V_g = -2$ V

Figure A2.22 – Conductance versus gate voltage of YB23 in vacuum and with saturated Ar pressure at $T = 50$ K

We measured the conductance of YB23 versus Ar pressure exposure at $V_g = -0.25$ V and -0.4 V, but did not obtain beautiful isotherms, see Fig. A2.23. It might correspond to the complex of the conductance depended on gate voltage and adsorbates.

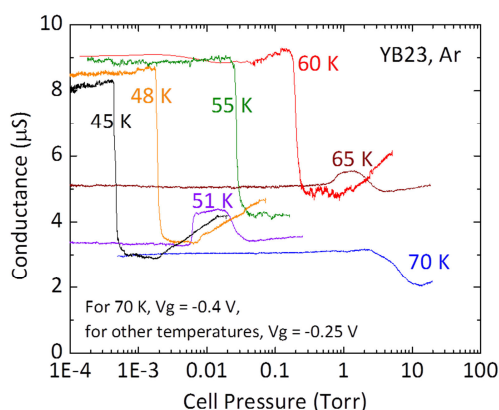


Figure A2.23 - Conductance isotherms of SWNT YB23 measured with Ar

Kr

The conductance versus gate voltage of YB23 in vacuum and with saturated Kr exposure is shown in Fig. A2.24. We measured the Kr conductance isotherms at $V_g = -1.3$ V, see Fig. A2.25. The shape of the isotherms looked more like YB12. The conductance did not decrease at first, but increased directly (a large riser) at the transition pressures. The transition pressures of YB23 Kr isotherms were close to the transition pressures of isotherms of YB10a, YB18, and YB19 at the same temperatures.

There were small steps in the isotherms before the conductance increased quickly, consistent with what we saw in YB23 Ar coverage isotherms. These small features also seemed to appear in YB12 Kr conductance isotherms. But we did not observe them in YB12 Kr adsorption isotherms.

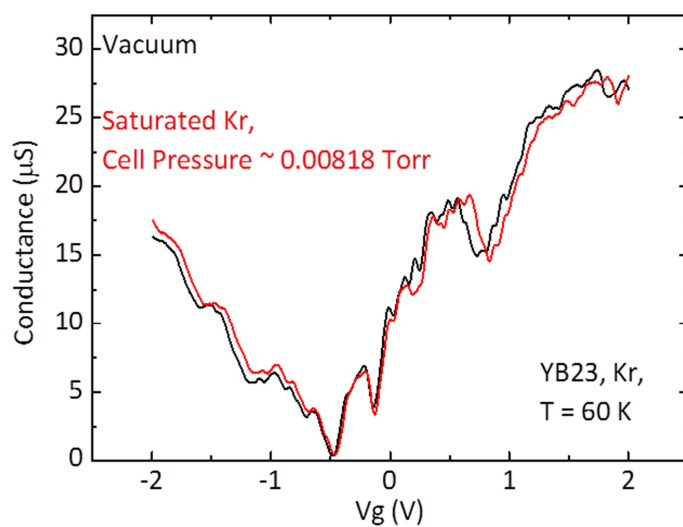


Figure A2.24 - Conductance versus gate voltage of YB23 in vacuum and with saturated Kr pressure at $T = 60$ K

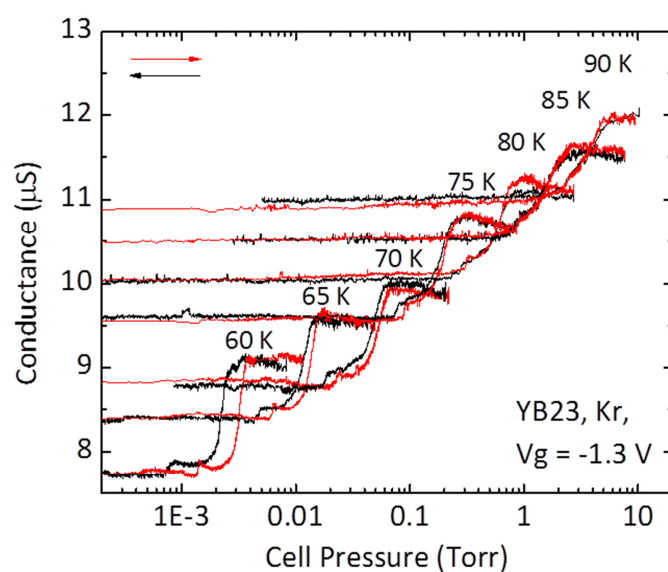


Figure A2.25 – Conductance isotherms of SWNT YB23 measured with Kr, $V_g = -1.3$ V

YB24

We measured YB24 with Ar and Kr. Most of the data was for the conductance. Only limited adsorption isotherms were obtained.

Ar

The conductance, Ar isotherms of YB24 at $V_g = -0.5$ V are shown in Fig. A2.26. The conductance decreased first, then increased (a large riser), and finally decreased again slightly. The pressures of the large risers of YB24 Ar conductance isotherms were close to the pressures of YB18, YB19, and YB23, slightly higher than the pressures of YB10a and YB11, and higher than YB16 at the same temperatures.

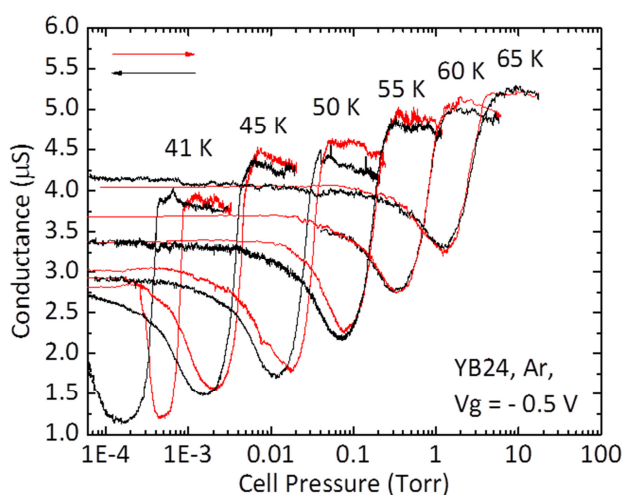


Figure A2.26 - Conductance isotherms of SWNT YB24 measured with Ar, $V_g = -0.5$ V

When we used significant different source-drain output voltage amplitudes for the adsorption and conductance isotherms, for example 5 mV for the coverage isotherms and 1 mV for the conductance isotherms, their transitions occurred at different pressures for the same temperatures, see Fig A2.27. It indicated that the power given by $V_{ds} \cdot I$ warmed up the device.

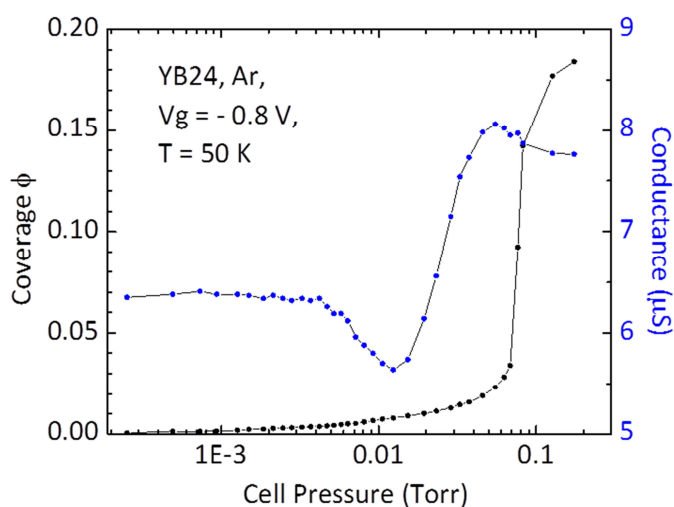


Figure A2.27 – Adsorption and conductance Ar isotherm of YB24 with different source-drain bias voltage amplitude at $V_g = -0.8$ V, $T = 50$ K

Kr

The conductance versus gate voltage of YB24 in vacuum and with saturated Kr exposure at $T = 75$ K is shown in Fig. A2.28.

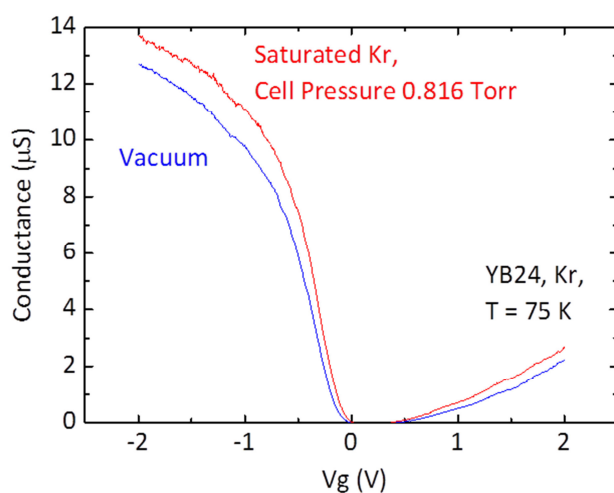


Figure A2.28 - Conductance versus gate voltage of YB24 in vacuum and with saturated Kr pressure at $T = 75$ K

Fixing $V_g = -0.3$ V, we measured the Kr conductance isotherms, see Fig. A2.29. Like the Ar isotherms, the conductance decreased first, then increased (a large riser), and finally decreased again slightly. The pressures of the large risers in the Kr isotherms of YB24 were close to the pressures of devices YB10a, YB18, YB19, and YB23 at the same temperatures.

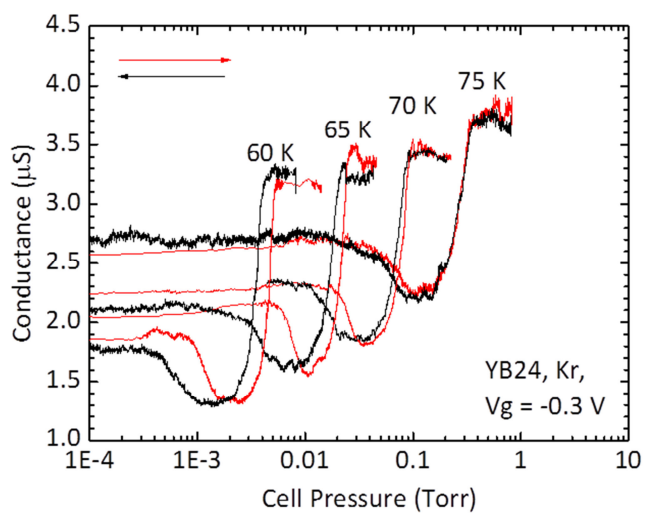


Figure A2.29 - Conductance isotherms of SWNT YB24 measured with Kr, $V_g = -0.3$ V

YB10

Device YB10 was measured with ^4He for 3 adsorption isotherms.

^4He

The ^4He isotherms of YB10 are shown in Fig. A2.30. The ^4He pressures at the middle of the isotherms of YB10 were higher than the ^4He pressures at the middle of the big shift of conductance peaks of YB14. It seemed that YB10 belonged to class 2 devices.

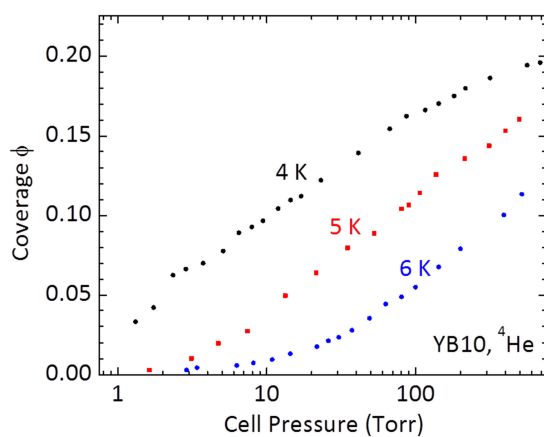


Figure A2.30 - Adsorption isotherms of SWNT YB10 measured with ^4He by Richard Roy

A3. Graphene

A piece of graphene was measured using the cryocooler. We studied adsorption on the pristine exfoliated single-layer graphene on a substrate by conductance isotherms measurements. The device was fabricated from graphene sheets by San-Feng Wu in Prof. Xiao-Dong Xu's lab without using any chemicals.

We obtained reproducible Kr isotherms at $T = 80\text{ K}$, $V_g = 0\text{ V}$, see Fig. A3.1. There is a large riser in isotherms of this graphene device like what we saw in the isotherms of SWNTs. The pressure where the riser happens in the graphene isotherms at $T = 80\text{ K}$ is between the riser pressures of isotherms of graphite and SWNTs at the same temperature, as shown in Fig. 5.3. Unfortunately, the device stopped working soon after these isotherms were obtained. More measurements are needed for study of adsorption on graphene.

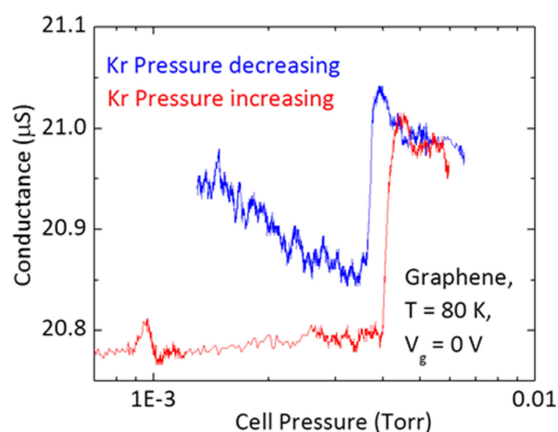


Figure A3.1 – Conductance isotherms on a piece of graphene with the pressure of Kr exposure increasing and decreasing at $T = 80\text{ K}$ and $V_g = 0\text{ V}$

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