ELECTRIC FIELD DETECTION BY ELECTROSTATIC FORCE MICROSCOPY
FOR CLOCKING QUANTUM-DOT CELLULAR AUTOMATA MOLECULES

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

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July 2006
Quantum-dot cellular automata (QCA) is an emerging, promising, future generation computational architecture that encodes binary information into the positions of electrons. The switching and logic function of this transistorless architecture has already been realized in metal QCA and magnetic QCA. “Bottom-up” molecular implementation may not only circumvent the lithography limits, but also realize room temperature operation, where metal QCAs could not function. A clock scheme is introduced to execute the pipeline calculation and provide the power gain. The clocking electric field can be produced by buried nanowires.

Electrostatic force microscopy (EFM) is a direct way to measure the electric field. In our experiments, parallel nanowires were fabricated by electron beam lithography and metal lift off, and applied with different voltages to simulate different clocking phases. The electric forces were measured by the phase signal of EFM. EFM-phase measurement is not well understood here and used mostly for phase-contrast qualitative measurements. We demonstrate quantitative EFM-phase measurements. Also, we discuss a source of error in EFM dual-pass measurement, which has been considered in our model for quantitative EFM-phase measurements. Finite element analysis is provided for applications of clocking QCA molecules. The simulations about
programmable logic array in QCA and low-power consumption of QCA clocking wires have been demonstrated.

Future work about the switching of molecular logic states by electric fields and detection by EFM or Kelvin probe force microscopy will be discussed.
DEDICATION

To my parents and my wife - Chunyan
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ACKNOWLEDGMENTS

First of all, I wish to thank my advisor, Prof. Bernstein, for his endless support, guidance, and encouragement. Thanks to his mentoring, I have benefited a lot from his experience. I am grateful for his patience and many suggestions throughout my graduate study and research. I enjoyed working with him and will cherish this experience forever in my life. I also wish to thank my other committee members including Prof. Porod, Prof. Lieberman, and Prof. Xing.

Highly appreciated are Prof. Lent, Prof. Snider, Prof. Orlov, Prof. Niemier, and Prof. Sharon Hu for helpful discussions in many group meetings. Special thanks to Qingling Hang, Wenchuang Hu, Jie Wu, Qing Liu, Jie Su, Heng Yang, and Ling Zhou, with whom I have had daily discussions. Equal appreciation goes to Alexandra Imre, Ravi Kummamuru, Kameshwar Yadavalli, Xiangling Luo, and other students, and lab manager Michael Thomas, and other administrators who give me advice and keep the laboratory running.

I am especially indebted to my parents and Chunyan for their encouragement. Without their contribution, this thesis would have been impossible. Finally, I am particularly grateful to Intel Corporation for funding.
CHAPTER 1
INTRODUCTION

The ability to innovate for downscaling CMOS is becoming increasingly more difficult. At the current rate of change, the power dissipation for CMOS circuits based on current-driven schemes will melt the chips. Quantum-dot cellular automata (QCA) [1-5] is one promising replacement for CMOS for its lower power consumption and possible implementation by molecules [6]. By clocking QCAs, power gain and pipelined operation can be achieved. The research presented here is to use electric force microscopy (EFM) to detect the electric field around the clocked nanowires. Part of the effort will be making nanowires by electron beam lithography (EBL), investigating the properties of the wires, and simulate the electric fields used for clocking QCA logic circuits.

A molecular QCA cell consists of two coupled three-dot molecules [7] as shown in Fig. 1.1. The size of the cell is on the nanometer scale. Due to Coulomb forces between dots inside the cell, there are two charge configurations for the top four dots, representing logic “1” or logic “0”. This polarity can influence neighboring cells by the same force. Cells try to align to each other. Thus the polarity can be transported along a QCA wire. Logic gates can be realized by QCA cells. For instance, as shown in Fig. 1.2, a majority gate can be easily implemented and four majority gates make a 1-bit full adder as shown in Fig. 1.3. The majority gate may be a basic logic element for large circuits.
The introduction of a clocking signal [9] addresses the power gain problem for molecular circuits. A weak input signal can be restored by the clocking signal. Also logic data flow can be directed in the desired direction and pipeline computation can be obtained. Supposing the charges on dots are all electrons, an attractive force, exerted by the underlying clocked nanowire with a positive voltage applied, will pull the electrons down; a repulsive force, exerted by the underlying clocked nanowire with a negative voltage applied, will push the electrons up. If the force is strong, the electrons will be in a “locked” state or “null” state. Between those two states, there is a “switch” state where electrons can move due to the force coming from neighboring cells. Logic computation occurs only at “switch” zones. For example, the electrons in the upper two drawings of Fig. 1.1 (b) feel a strong force and are in a “locked” state while the electron at the bottom drawing is in a “null” state. In Fig. 1.1 (c), the electrons are either in “locked” states or in “switch” states.

In Fig. 1.2 (c), the size of nanowire for clocking circuits is not in scale with the above molecules. In reality the nanowire can be dozens of molecules wide. The materials for the nanowire can be metal or even carbon nanotubes. Carbon nanotubes are difficult to grow to form clocking circuits at specified places. For our research, metal nanowires are fabricated with top-down electron beam lithography. The Hitachi FESEM EBL system built by Wenchuang Hu [10] can guarantee 25 nm metal wires as shown in Fig. 1.4 (a). However, due to the metal grain size and the roughness of PMMA trenches, metal nanowires after lift-off are often discontinuous, which makes the nanowires unable to conduct current, which will be discussed in Chapter 7. As shown in Fig. 1.4 (b), below 10 nm most metal wires cannot get lifted-off, even though the top surface of the PMMA trenches looks acceptable. Possible solutions to this problem are the adoption of cold developing PMMA [10], using metal or alloy with small grain size, and adoption of ultrasonically-assisted developing PMMA [11].
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Fig. 1.2. A majority gate with a clocked circuits. (a) Schematic representation of a majority gate. Three inputs are “1”, “1” and “0”. The output is “1”. (b) Corresponding molecular QCA majority gate. (c) Underlying the molecular layer is a clocking signal layer. Nanowires can be applied with voltages of different phases.
Fig. 1.3. Logic data flow of a one-bit full adder with an underlying clocking circuit (adapted from [8]). (a) Schematic representation of a one-bit full adder is shown. “M” means majority gate. A, B and $C_{i-1}$ are inputs. $S$ and $C_i$ are outputs. (b)-(e) Time evolution of data flow. The cells in blue column for each are fixed and act as inputs. The inputs and outputs correspond to those in (a). Here, A, B and $C_{i-1}$ are logic “0”, logic “1” and logic “1” respectively. The cells in green are at logic “0” while the red cells are in logic “1” and the white cells are logic “null”. The brightest and darkest columns are regions where the electric forces are greatest. The cells in the brightest column are in the “locked” state while the cells in the darkest column and with two-column distance are in the “null” state. The cells in “switch” region occupy about two columns between the “locked” region and the “null” region.
Fig. 1.4. Metal nanowires after lift-off by the Hitachi EBL system (adopted from [10]). (a) 25 nm gold wires are shown with gold grain size at about 8 nm. (b) Only two sub-10 nm nanowires are seen.

For the present, there is no alignment capability in the Hitachi EBL system. The device can be connected out by “mix-and-match” method that will be discussed in Chapter 4. With recently purchased commercial EBL system, Elionix 7700 EBL system, we can obtain sub-10 nm features as shown in Fig. 1.5. The system boasts a 75 kV ZrO/W thermal field emission electron gun and the overlay accuracy or the stitching accuracy below 40 nm. However, the problem of discontinuous metal wires after lift-off still exists. Fig. 1.6 shows electric force microscopy (EFM) imaging of clocked or charged nanowires. The clocked nanowires were made by the Amray EBL system. Chapter 2 talks about the QCA history and recent development of QCA devices. The principle of EFM, the electric field detector, is summarized in Chapter 3. Other EBL results and qualitative EFM measurements are discussed in Chapter 4. The Amray EBL system can produce around 30 nm nanowires, but cannot compete with the Hitachi EBL system. However, using the Amray EBL can connect our nanodevices made by the Hitachi EBL to outside micron-size pads. For the simulation of electric fields emitted from clocked wires, commercial finite element analysis software, FEMLAB, is used [12] to compute the electric field distribution at the plane of QCA molecules.
Fig. 1.5 SEM picture of PMMA resist after developing and exposure under Elionx 7700 EBL system. The PMMA trench is about 4.8 nm wide. The dose is 0.7 us/dot.

X. S. Hu, et. al proposed an implementation of a programmable logic array (PLA) by QCA cells [13]. Special metal pads are designed to hold the select bits of the PLA cells. Electric fields produced by these metal pads are simulated by FEMLAB. The holding properties of the special metal pads have been demonstrated in Appendix B.

Another issue is the power consumption of the clocking circuits, which accounts for most of the power consumption of molecular QCA circuits. The power is dissipated through charging and discharging the clocked nanowires. To calculate the power consumption, we need to know the capacitance of the nanowires, which depends on their geometries, the material for metal wires, and the material for insulating layers. Appendix A presents some simulation results of power consumption. Also, the influence between nanowires due to different clock phases cannot be ignored.
Fig. 1.6. SEM, AFM and EFM imaging of clocked nanowires. (a) A SEM picture of nanowires. The nanowire is about 70 nm wide. The pitch is 300 nm. (b) Corresponding AFM picture. (c) Corresponding EFM picture. For picture in (c), the tip is in EFM mode with the lift height at 60 nm. From the top, the voltages applied to the nanowires are 1.4 volts, 0 volt, -1.4 volts, 1.4 volts, 2.8 volts and -2.8 volts. The brightest color in the picture corresponds to the electric field intensity at $4.67 \times 10^5 \text{ V/cm}$.
In Chapter 5, we investigate a source of error in EFM phase measurement [14]. EFM does dual-pass operation: during the first scan, the system records the topography; during the second scan, the system records the phase signal while lifted at a specified constant height. Our experimental results shows that the residual electrostatic force during the first scanning can alter the actual topography, which is critical for quantitative EFM phase measurements [15]. For most tip-sample models, the sample is modeled as an infinite surface, which is not true in our case. A simple tip-sample model is presented that explains the experiment very well. Taking this source of topography error into account, we proposed a new way to realize the quantitative EFM phase measurements in Chapter 6. These experiments are the first to demonstrate quantitative force measurements based on phase information in EFM.

In summary, the contribution to QCA development is to investigate the electronic properties of nanowires and detect the electric field by EFM quantitatively for the purpose of clocking molecular QCA. Also in the future we will use EFM to detect the switching of QCA molecules under electric field as discussed in Chapter 7. For other QCA design software, QCACWEST is used to design clocking signals [8]; M-Aquinas uses the clocking signal to drive the logic computations [8]. A possible improvement of QCACWEST is to reduce the computation complexity. QCACWEST computes incoming contributions from all nanowires. Since the intensity of the electric field is inversely proportional to the square of the distance from the nanowire, the electric field inside the molecular layer comes mostly from the nearby nanowires. Thus, calculating electric field with a few nanowires will reduce the computing time without much deviation from the results had they included contributions from all nanowires.
2.1 Beyond CMOS devices

According to (Gordon) Moore's law, the density of transistors on integrated circuits (ICs) doubles roughly every 24 months [1]. The trend in this scaling will come to a stop due to physical limits of solid state electronics. The heat generated by billions of transistors cannot be dissipated quickly enough to prevent the damage. For the physical limits, there are some temporary solutions. For the signal delay with the shrinking of interconnect wires, copper has taken the place of aluminum due to its low resistivity and superior resistance against electromigration [2] and low $k$ interlayer dielectric is being adopted to reduce the coupling capacitance between layers [3]. High $k$ material will be used for the gate insulator instead of silicon dioxide because a silicon dioxide insulator would allow excessive leakage current when the gate thickness is below a few nanometers [4]. Also, strained silicon [5] can be exploited to increase the carrier mobility along the channel. Novel materials and process innovations can bring the gate node below 50 nm where a new nanotechnology era begins. In addition, perhaps the FinFET [6-7] can sustain Moore’s law until 2010 when the gate node will measure at 45 nm (70 nm for today’s gate node). However, in the long term the technology based on CMOS will lose momentum, calling for devices beyond the CMOS roadmap.
The single electron transistor (SET) is important to the development of quantum-dot cellular automata (QCA). The common force for SETs and QCA is the Coulomb force. Tunnel junctions for SET can be used for tunnel barriers between dots in metal QCA. SETs can be used as sensitive electrometers for detecting electrons on metal QCA dots. Metal QCA and SET can be fabricated on the same chip with the same process, which facilitates the experimental demonstration of QCA devices.

The single electron transistor [8, 9] may be a possible substitute for CMOS. The operation of SET is based on coulomb blockade principles. SETs boast low power consumption since they manipulate only a few electrons and exhibit extremely high sensitivity. SETs can be used for logic computation [10], for example, a single-electron inverter [11]. For practical applications now, single electron devices are mostly used for high density memory [12]. SETs can combine with MOSFETs to make hybrid devices embracing the low power consumption properties of SETs and the high speed of MOSFETs [13].

2.2 QCA history

For a dozen years’ investigation into QCA devices, we have witnessed great progress in the development of metal QCA, including primitive QCA cells, QCA wires and QCA latches, and the introduction of the clock scheme and magnetic QCA. Recently, interest has developed in possible molecular implementation of QCA devices.

2.2.1 Metal QCA

The concept of QCA, for which ground state computation significantly reduces the power dissipation and encodes binary information into the charge configuration, originated in 1993 [14]. At that time, a QCA cell was conceived as a molecule with five islands. How to make a wire with QCA cells and how to compute with QCA cells, for
instance, how to arrange QCA cells functioning as AND, OR, and inverter logic gates, had been solved only theoretically.

The QCA concept is actually a brand new circuit concept. The islands or the dots of QCA can be metal or molecules. So far, the primitive concept has undergone two changes. First, five-dot QCA cells became two two-dot or three-dot QCA half cells [15]. Second, a clock signal was introduced to enhance the edge-driven scheme [16]. The diminishing signal after several logic computations or just propagation along a QCA wire is restored to the initial state by the clock signal, which solves the power gain problem plaguing the non-clocking edge-driven scheme. For experimental innovations of QCA devices, the convenient fabrication of QCA is made possible with the choice of aluminum instead of AlGaAs/GaAs [24]. Aluminum SETs can be sensitive charge detectors for aluminum quantum dots made on the same chip [18], as shown in Fig. 2.2 (a). Also, as shown in Fig. 2.2 (b), “honeycomb” shaped charging diagram for coupled double quantum dots can be used for distinguishing electron states [19]. Successful external charge state detection of a double-dot system makes QCA devices possible [20] [21], as shown in Fig. 2.2 (c).

Thus, the logic devices proposed [14] can now be experimentally demonstrated. A functional QCA cell, as shown in Fig. 2.3, was verified by the nonlinear switching properties of coupled double-dots [22, 23].

A six-dot QCA cell was demonstrated [24], followed by a QCA binary wire [25]. The QCA majority logic gate was presented by I. Amlani et al. [26], though the adjacent input cells were simulated by applied potentials.
Fig. 2.2. Two previous works critical for experimental QCA and successful external detection for double-dot system (adopted from [18, 19, 20] respectively). The square box symbol represents a tunnel junction. (a), Aluminum SET can detect charge on an aluminum quantum dot by the capacitive-coupled method. The SET and the quantum dots are coupled by the capacitor $C_c$ in the top picture of (a), corresponding to the capacitor formed by wire b and wire m at the bottom. (b) Scheme for detecting charge state on double-dot system. Charges in dots $n_x$ and $n_y$ are moved adiabatically one by one by two applied gate voltages at top. Charge configuration as the function of two gate voltages is shown at bottom. The states following the circle are (0,0), (1,0) and (0,1). (c) Charge states on a double-dot system, actually a QCA half cell, was detected with two SETs with the scheme in (b). The “honeycombs” can be drawn with the mapping of conductance through $D_1$ and $D_2$ as the function of $V_A$ and $V_B$. By $C_{D_1-D_2}$ and $C_{D_2-D_4}$, the conductance changes through two SETs reflect the potentials of $D_1$ and $D_2$, which correspond to charge states on this double-dot system.
Fig. 2.3. Schematic and SEM pictures of a QCA cell (adopted from [23]). (a) Schematic of a QCA cell with the bottom pictures in detail. The difference from Fig. 2.2 (c) is that the inputs for dots $D_3$ and $D_4$ are not bias voltages but dots $D_1$ and $D_2$. (b) SEM picture of a QCA cell.
2.2.2 Clock scheme

The introduction of the clock signal was a great improvement in QCA architecture [16] [27]. A multiple-phase clocking signal is applied to move the logic information, i.e. charge configuration, along the QCA wire. Logic computation takes place at the junctions of the QCA wires at the proper clocking time. These junctions are corners or crosses. The principle of this clocking scheme bears some resemblance to that of charge coupled devices (CCD), except that the charge configuration is shifted instead of the charge produced by photons in the CCD. Not only can power gain be achieved, but also pipelining computation can be realized with this clocking scheme.

We can lay down several QCA cell nets. Each net conducts a particular logic computation. With inputs on, the clock signal will drive cells to compute at the same time. Also at different times, we feed in different inputs. Thus, at any time there are several logic computations going on even along one net. That is the principle of pipelining that can enhance the data output. The single electron switching due to the new clocking function was experimentally demonstrated in a QCA half cell [28]. Multiple tunnel junctions were introduced to land electrons to remain long enough on dots in order to get the function of a latch [29]. A shift register [30] consists of several latches depending on the number of the bits of address. A pseudo multi-latch shift register was experimentally proven, resulting in power gain [31]. “Pseudo” here means that the first and the third are actually the same because the second latch was used as the input to the first latch. This experimental technique was applied to the majority gate previously made [26], as shown in Fig. 2.4.

What kind of difficulty arises when we add another latch, as shown in the shadow box of Fig. 2.4, that consists of $D_2$, $D_8$ and $D_9$. The clock signal $V_{c2}$ has to be from another level, which requires a two-level, interconnecting nanocircuit. The
problem can be circumvented by using the first latch as the third latch. Multiple tunnel junctions are used to reduce the probability of co-tunneling.

2.2.3 Magnetic QCA

Binary information can also be encoded into the magnetization state of ferromagnetic materials [32, 33], such as supermalloy like Ni$_{80}$Fe$_{14}$Mo$_{5}$X$_{1}$ [32], where X is other metals, and polycrystalline NiFe [33], to implement QCA concepts. Instead of quantum mechanical electron tunneling between quantum dots as shown in aluminum QCAs, i.e. electrostatic QCA (EQCA), magnetic QCAs (MQCAs) exchange interaction of spins between nearby single-domain magnets.

![Schematic pictures of a majority gate and a shift register](image)

**Fig. 2.4.** Schematic pictures of a majority gate and a shift register (adopted from [22] and [30] respectively). (a) Inputs A, B and C coming from bias voltages, which act as the nearby cells. (b) The difficulty of adding another latch in shadow that consists of $D_7$, $D_8$ and $D_9$. 
As shown in Fig. 2.5, there are two MQCA networks. Each network consists of 69 circular dots made from $Ni_{15}Fe_{14}Mo_{5}X_1$. These dots are 10 nm thick, 110 nm in diameter, and 135 nm in pitch. The magnetostatic interaction energy between two of these dots is $5.2 \ eV$, which is much greater than room temperature energy at $26 \ meV$. MQCA can realize room temperature operation without scaling down to the sub-10 nm region.

![Fig. 2.5 SEM picture of MQCA network fabricated by Cowburn and Welland. (a), (b) and (c) are SEM imaging of the left, the center, and the right of the MQCA networks. (adopted from [33])](image)

The elongated dots in Fig. 2.5 (a) are used to inject signals into the network because of its inertia to the influence of neighboring dots. Only two magnetization states are stable: leftwards and rightwards. The switching of the magnetization state is detected by a magneto-optical measurement. For current research on MQCA, shape-induced anisotropy is introduced to separate the magnetic vector directions of magnetic solitons and the propagation of binary information of these solitons [33]. Also magnetic force microscopy (MFM) is used to obtain the phase contrast of two magnetic vector directions of magnetic solitons. The paper assumes that phase imaging of two magnetic solitons can represent binary logic states as shown in Fig. 2.6. SEM pictures of those magnetic solitons are shown in Fig. 2.7 (a). These nanomagnets made by EBL and permalloy lift-off are 70 nm wide, 135 nm long, and 30-nm permalloy thick.
Fig. 2.6 Magnetic force microscopy (MFM) imaging of two stable magnetic states of solitons.

Fig. 2.7 (a) SEM picture of MQCA wire; (b) MFM picture of polarized MQCA wire where the nanomagnets circles acts as the driver. (adopted from [33])
The gap between nanomagnets is 25 nm. A corresponding MFM picture is shown in Fig. 2.7 (b), where the nanomagnet circled acts as the driver for the whole chain of nanomagnet.

The logic information is transported leftward by the interaction between adjacent magnetic solitons, which functions as a QCA wire.

In addition to the QCA wire, a universal logic gate, i.e. the majority gate, has been demonstrated. Three horizontally elongated magnets as shown in Fig. 2.8 (a) act as the driver magnets. Four vertically elongated magnets acts as the whole majority gate, where the output magnet is the rightmost. The central magnet is coupled with the output magnet as one magnetic soliton. The logic states of these two magnets are always opposite. Thus, different from the traditional majority gate, we can call not-Majority gate.
Fig. 2.8 (a) SEM pictures of different locations of driver magnets and the majority gate; (b) MFM imaging of different combination of logic inputs functioning as a Majority gate. (adopted from [33])
2.2.4 Molecular QCA

Molecules and metal nanoclusters are naturally grown. Their sizes are beyond the current lithography resolution. They can be used to make real devices, such as carbon nanotube field effect transistors [34-36]. Even SETs can be made by bending a single wall carbon nanotube (SWNT) twice by an atomic force microscopy (AFM) tip [37]. Each bend works as a tunnel junction. Molecules could be used for QCA devices if there are dots which electrons can hop [38]. For instance, the redox sites in a molecule act as good electron containers. A QCA half cell can be a three-dot molecule [39, 40], as shown in Fig. 1.1. The three dots form a “V” shape. The upper two dots plus another two dots from another molecule can interact with each other by Coulomb forces. The bottom dot acts as an intermediary site when electrons hop from one top dot to the other. These molecules can be aligned to obtain a logic majority gate as shown in Fig. 1.2. Two-dot QCA half cells, for instance, a Fe-Ru complex, are still under investigation [41, 42].

Fig. 2.9 is a diagram for an ideal test structure for a single molecule QCA cell. It is a four-terminal QCA cell with four metal nanoelectrodes attached and with a clocked nanowire running across the middle of the cell. The whole system is under the influence of the electric field emitted by the underlying clocked wire. The size in the diagram is not to scale. The width of the clocking wire can be dozens of cell sizes. The logic state is logic “1”. We can apply a negative voltage $V$ to $pin_3$ with the other pins grounded. Usually $+V/2$ is applied to $pin_3$ and $-V/2$ is applied to $pin_4$. Assuming it is in the “switching” zone, the electron in $D_4$ will pass $D_5$ and arrive in $D_6$. Due to the Coulomb force from the electron in $D_6$, the electron in $D_3$ will move to $D_1$. The system will be in equilibrium again but now in logic state “0”. The charges on the dots can be detected by SET electrometers with coupled capacitors.
Two charge detectors are indispensable for the test. The alignment of the cell to electrodes and detectors will be a big obstacle. For the test of an Fe-Ru complex, we can use nanogaps instead of a scanning tunneling microscope (STM) for molecule measurement [41]. A nanogap can be made by shadow evaporation plus electromigration [43, 44] or the mechanical controlled break junction (MCB) method [45, 46]. The QCA half cell can sit inside the gap, and the particular phenomena for tunneling through double quantum dots can be observed.

We also can lengthen the molecule by adding more dots to relax the distance constriction of nanogap. The particular effect for tunneling through multiple tunnel junctions can also be obtained. For final devices, we can fabricate several rows of self-assembled molecules in parallel. There are two advantages: first, it can fulfill the fault-tolerant design [47]; second, it can relax the alignment from the detectors to the outside nanoelectrodes.
2.3 Nanowire fabrication and electron beam lithography

There are many ways to fabricate metal nanowires including chemical synthesis, self-assembly, templated deposition and lithography methods [48]. For chemical synthesis and self-assembly [49], the resulting metal nanowires are difficult to grow at specified locations. For templated deposition, MBE-defined templates [50, 51] can be used for nanoinprint lithography as the mold [52], which has a broader application field compared with the step-edge templates [53]. These two template methods are appealing because the resolution depends on the thickness of the film used for templating. The thickness can be easily reduced to the angstrom level.

There are many reports about nanowire fabrication by EBL [54-57]. These nanowires are usually isolated and the high-resolution pictures of exposed and developed resist show only trenches in the resist, which creates the illusion of high-resolution EBL. The resolution of EBL should be gauged by the width of the metal nanowire after lift-off and the pitch, the distance between nanowires [58, 59]. The bottleneck for the extremely narrow metal wires is not the beam size since most electron beam sizes are far below the resolution than can be achieved [60], but is the resist, the developer and the development process [61-66]. The grain size of metal polycrystalline cannot be ignored because some metal grain sizes are about 10 nm, which makes it difficult to make a conductive wire.

The electron beam resist for common use is polymethyl methacrylate (PMMA). PMMA can be used for positive or negative tones [67]. Other negative electron beam resists like hydrogen silsesquioxane (HSQ) [68] and calixarene [69] can be used for fabrication of nanowires. For the resolution, they cannot compete with PMMA in positive tone [63]. However, the negative resist can be used as the etch mask for an underlying metal layer that has already formed a compact polycrystalline structure. After reactive ion etching (RIE), a conductive nanowire even with large grain size can be hopefully obtained. The processes for positive or negative resists are shown in Fig. 2.10.
2.4 Electrostatic force microscopy

EFM has many applications in semiconductors [70]. It can detect contact potential differences, which can detect P-N junctions and active LED regions. Kelvin probe microscopy (KPM), an extension of EFM, can measure surface potentials and get absolute voltages of our clocked nanowires. One appealing characteristic of EFM is the ability to inject charge on the surface and detect it at once at room temperature [71, 72]. The characteristic and the principle of EFM will be discussed in Chapter 3.
Electrostatic force microscopy is a useful tool to detect and measure the electric field emitted from clocked wires [73]. The wires can be carbon nanotubes (CNT) or metal nanowires. Carbon nanotubes not only can work as devices used on its semiconductor properties, but also can be used as interconnecting wires used on its high carrier mobility and the metallic properties. CNTs could be suitable for clocking molecular QCA cells. Recently, we have been making metal nanowires. 10 nm or smaller nanowires can be achieved with our current field emission EBL system [74]. In the near future, it may be possible to grow carbon nanotubes at particular locations on these nanowires. A uniform electric field prevents any pre-bias settings for molecular QCA cells before the arrival of clocking signals. We can put arrays of QCA cells onto the proper regions. The principle of EFM will be discussed in Chapter 3. Though the electric force gradient instead of the electric force is detected by our EFM, electric force gradient detection has better lateral resolution than the electric force detection [75, 76].

We can use the smallest EFM tip based on a carbon nanotube [77] to switch the state of the QCA cell. EFM can detect optically-induced molecular switching [78] and even the single electron state on quantum dots as shown in Fig. 2.11 [79]. In Fig. 2.11 (a), \( V_{tip} \) was applied to the EFM tip. In Fig. 2.11 (b), the black curve was obtained by scanned gate microscope (SGM), which scans over the sample surface with a biased tip while recording the sample conductance. At the peaks of both curves, an electron is added to the quantum dot. Those Coulomb oscillations show that the charge state on the quantum dot can be detected by the transport properties. It will be a very good solution to the initial states problem of molecular QCA cells if these molecules can be optically flashed. Photosystem I reaction center may be a choice for QCA molecule [80].
2.5 Molecular patterning

Although we can grow as many molecules as we want by self-assembly, the molecules usually cannot form useful patterns by themselves. For instance, they cannot develop into a pattern of a majority gate as shown in Fig. 1.2. If we can manipulate molecules in particular patterns as discussed in Chapter 1, the molecules can realize certain logic functions. How to arrange molecules in particular patterns is important to the implementation of molecular QCAs.

![Diagram of a single-wall carbon nanotube quantum dot](image)

(a) A single-wall carbon nanotube attached to metal contacts and tunnel junctions are formed by defects. (b) The black curve for the conductance change of the nanotube quantum dot as the function of the tip voltages and the red for the force sensed by the EFM tip as the function of the tip voltage.

Fig. 2.11. Nanotube quantum dot measured by EFM at 0.6 K (adopted from [79]).

For a direct method, researchers either “draw” molecules on the gold surface by an AFM tip, which is called dip-pen nanolithography (DPN) [81]; for an indirect method, metal tracks are paved before dipped into the solution of molecules and molecules will grow on these tracks. For instance, $C_{18}SH$ molecules assemble on the gold surface [82]. However, these underlying gold surfaces will possibly short-circuit the devices.
Q. Hang et al. [83] have demonstrated the molecular patterning of 
\[ \left[ (NH_3)_3 Ru(pyrizine)Ru(NH_3)_3 \right] \cdot o - tolunesulphonate \] (CT5), a candidate for QCA molecule [38], on a SiO_2 surface. The device patterns were drawn by electron beam lithography in PMMA resist. After development, PMMA trenches were formed. The CT5 molecules were deposited directly from the solution into trenches. Then the rest of the resist was washed away by using dichloromethane (DCM) instead of acetone [84]. The AFM picture of CT5 molecules is shown in Fig. 2.12. The average height for CT5 is 0.9 nm.

In summary, QCA is a promising computational architecture beyond CMOS devices. Logic QCA devices have been experimentally demonstrated. Great progress has been made in metal QCAs, magnetic QCAs, and molecular QCAs. We introduced EBL nanofabrication methods, molecular patterning, and the detection of electric field by EFM. In the next chapter, the principles of EFM will be discussed in detail.

![Fig. 2.12. Tapping mode AFM imaging of CT5 molecules (adopted from [83]).
(a) The AFM picture of four CT5 molecular wires. (b) The cross sectional analysis of (a).](image)
CHAPTER 3
DETECTING ELECTRIC FIELD: PRINCIPLE OF ELECTRIC FORCE
MICROSCOPY

3.1 Introduction

Electric force microscopy (EFM) can detect electric fields directly. An understanding of operation principle of EFM will help in interpretation of the experimental results. First, we introduce the operation of EFM and discuss electric force gradient measurements. Second, we introduce Kelvin probe microscopy (KPM), an extension of EFM, and investigate the surface contrast transfer mechanism. Last, we discuss single electron detection and high speed detection by EFM.

3.2 EFM operation

EFM is one of modes of our multi-mode scanning probe microscopy (MMSPM) [1]. As shown in Fig. 3.1, the operation can be described in two steps. For the first step, we obtain a topography imaging by tapping-mode scanning. The software memorizes the topography from the first scan. For the second step, the cantilever is lifted up just above the sample at a specified distance. The probe scans over the sample following the curve of the topography. The geometrical effect is then compensated.
Fig. 3.1. Principle of lift-mode and the circuits for EFM (adopted from [1]). (a) Lift-mode method. (b) Circuits special for EFM.
3.3 Electric force gradient measurement

First, we apply principle of virtual work to get an electric force between the tip and the sample which are modeled together as a parallel-plate capacitor. Second, the tip-cone-cantilever model is introduced and the electric force is shown to have components from the tip, the cone, and the cantilever. Last, we derive the force gradient when the cantilever oscillates at the resonant frequency.

3.3.1 Principle of virtual work

When we apply a non-zero voltage to a conductive sample and ground the EFM probe, opposite charges will build up both on the tip of the probe and on the area of the sample that is close to the tip. Thus, the tip and the sample function as a capacitor. We model the capacitor simply as a parallel-plate capacitor as shown in Fig. 3.2. The force between the tip and the sample can be simulated as the force between two plates of the capacitor. We apply the principle of virtual work [2] to obtain the force between the two plates. In Fig. 3.2, assume the distance between the two conductive plates is $Z$ and the area of the plate is $S$. The electrostatic energy to charge the capacitor is

$$W_e = \frac{1}{2} C V^2 \text{ or } \frac{1}{2} \frac{Q^2}{C},$$

(1)

Fig. 3.2. Principle of virtual work: a parallel-plate capacitor.
where \( C \) is the capacitance of the tip and the sample; \( V \) is the voltage applied to the capacitor; \( Q \) is the corresponding charge on the capacitor. The attractive force \( F \) between the two plates can be derived by the principle of virtual work. Assume a very small displacement of \( dZ \) of the upper plate under the force of \( F \). The virtual mechanical work done by \( F \) is [2]

\[
dW_m = FdZ. \tag{2}
\]

The derivative of the electrostatic energy in the direction of \( Z \) is

\[
dW_e = \nabla W_e dZ. \tag{3}
\]

According to the principle of energy conservation,

\[
dW_s = dW_m + dW_e + dW_i, \tag{4}
\]

where \( dW_s \) is the work done by an outside source; \( dW_i \) is the loss of electrostatic energy. From Eq. (2)-(4), we get

\[
\partial W_s - \partial W_e - \partial W_i = 0. \tag{5}
\]

For a less perturbed system, \( dW_i \) can be ignored. Eq. (5) can be reduced to

\[
F = \frac{\partial}{\partial Z} W_s - \frac{\partial}{\partial Z} W_e. \tag{6}
\]

Consider the two cases of a fixed charge and a fixed voltage. For the case of the fixed charge, there is no outside source, so the first term on the right side of Eq. (6) is zero. With Eq. (4), we obtain

\[
F = -\frac{\partial}{\partial Z} \left( \frac{1}{2} \frac{Q^2}{C} \right) = \frac{1}{2} \frac{\partial C}{\partial Z} V^2. \tag{7}
\]

For the case of the fixed voltage, some charge \( \Delta Q \) flows due to the change of capacitance. The work done by the outside source is

\[
W_s = \Delta QV = \Delta CV^2. \tag{8}
\]

\( W_s \) is exactly twice \( W_e \). With Eq. (4), we get

\[
F = \frac{\partial}{\partial Z} \left( \frac{1}{2} CV^2 \right) = \frac{1}{2} \frac{\partial C}{\partial Z} V^2. \tag{9}
\]

We get the same results from the two cases. For our experiments, the nanowires are connected to a voltage source. The voltage is fixed. So the case of the fixed voltage

\[
\text{...}
\]
is used. For isolated charges on a sample surface, the case of the fixed charge can be applied.

3.3.2 Tip-cone-cantilever model

An EFM probe, either a highly doped silicon probe or a thin metal film covered probe, consists of three parts: a tip, a cone, and a cantilever. The models [3-5] for the EFM probe usually include three corresponding components as shown in Fig. 3.3. In those models, the sample surface is conductive and infinite. Each part is capacitively coupled to the sample surface in parallel. The total capacitance is

\[ C = C_{\text{tip}} + C_{\text{cone}} + C_{\text{cantilever}}. \]  

(10)

The total force also comes from three parts,

\[ F = F_{\text{tip}} + F_{\text{cone}} + F_{\text{cantilever}}, \]  

(11)

where \( F_{\text{tip}} = \frac{1}{2} \frac{\partial C_{\text{tip}}}{\partial Z} \nu^2 \), \( F_{\text{cone}} = \frac{1}{2} \frac{\partial C_{\text{cone}}}{\partial Z} \nu^2 \), and \( F_{\text{cantilever}} = \frac{1}{2} \frac{\partial C_{\text{cantilever}}}{\partial Z} \nu^2 \).

Fig. 3.3. An EFM probe consisting of three parts: a tip, a cone and a cantilever.
The diameter of a tip is about 10 to 30 nm and the length of a cantilever is 100-200 μm. At a very short tip-sample distance, \( F_{\text{cantilever}} \) can be neglected; while at some distance that depends on the geometry of the probe, \( F_{\text{cantilever}} \) may be greater than \( F_{\text{tip}} \) [4, 6]. In order to achieve high sensitivity, Jacobs suggested using a blunt tip instead of a sharp one to make a good coupling between the tip and the sample [7]. Thus \( F_{\text{tip}} \) stands out from the other two components. However, in order to get a high lateral resolution, the diameter of the tip should be very small; for instance, a carbon nanotube tip [8].

The advent of AFM at IBM [9] was an improvement over scanning tunneling microscopy (STM) because AFM can image non-conductive surfaces while STM cannot. Martin [10] did the first work on EFM at IBM. In Martin’s model, the capacitor of the tip and the sample was simply modeled as a parallel-plate capacitor,

\[
C = \varepsilon_r \varepsilon_0 \frac{S}{Z} ,
\]

where \( \varepsilon_r \) is the relative permittivity of the dielectric layer between plates and \( \varepsilon_0 \) is the dielectric permittivity in vacuum. \( \varepsilon_r \) is 1 since between the tip and the sample there is only ambient air.

Taking Eq. (12) into Eq. (9), the force is expanded as,

\[
F = -\frac{1}{2} \varepsilon_r \varepsilon_0 \frac{S}{Z^2} V^2 .
\]

In Martin’s experiment, the probe was working at its resonant frequency. The phase or frequency shift is proportional to the force gradient. The lateral resolution and the sensitivity were greatly enhanced. Details about the force gradient measurement will be covered later in this chapter. At a certain distance, the model of a parallel-plate capacitor gives the same results as the complex model of the tip-cone-cantilever.

Exploiting the distance, the simulation including the von der Waals force was simplified [11].
A real tip of an EFM probe looks mostly like a part of a sphere or parabola as shown in Fig. 3.4. We apply a non-zero voltage to a conductive sample and ground the tip. Between the tip and the sample, Poisson’s equation,

$$\nabla^2 V = -\frac{\rho}{\varepsilon_r \varepsilon_0},$$  \hspace{1cm} (14)

where $\rho$ is the charge density, is reduced to Laplace’s equation,

$$\nabla^2 V = 0.$$  \hspace{1cm} (15)

Laplace’s equation plus the boundary conditions of the tip and the sample can uniquely determine the distribution of electric field. We can solve the equation easily by numerical methods. However, it is hard to get an analytical solution. Hudlet et al. [3] presented a pseudo-analytical solution. The main idea for the solution is shown in Fig. 3.4. For one small area $dS$ centered at a point of $P$ on the tip surface, we draw a tangent line through $P$. The line intercepts the sample surface at a point $X_0$. An arc centered at $X_0$ with a radius of $PX_0$ intercepts the sample surface at $P'$. This arc is the electric field line from $P$ to $P'$. It is perpendicular to the surfaces of the tip and the sample. We get the intensity of the electric field from $P$ to $P'$,

$$E_{P\rightarrow P'} = \frac{V}{l_{P\rightarrow P'}},$$  \hspace{1cm} (16)
where $l_{P \to P'}$ is the length of the arc from $P$ to $P'$.

Also the capacitance for such a small parallel-plate capacitor from $P$ to $P'$ is

$$dC = \frac{\varepsilon_0 dS}{l_{P \to P'}}. \quad (17)$$

So summing all small parallel-plate capacitors on the surface of the tip, we obtain

$$C_\Sigma = \int_S dC = \int_S \frac{\varepsilon_0 dS}{l_{P \to P'}}. \quad (18)$$

Once we get the total capacitance in an analytical form, we can use Eq. (9) or Eq. (11) to get the force.

### 3.3.3 Electrostatic force gradient

We choose the electrostatic force gradient signal as the source of detection because it can improve the lateral resolution [12]. In our EFM, an EFM probe oscillates at the resonant frequency of the cantilever of the probe. When the EFM probe scans over a surface, what the probe detects is the force gradient rather than the force itself. In order to clarify the improvement on the lateral resolution, we start with a lumped oscillator system as shown in Fig. 3.5. The system is described by the following equation,

$$m \frac{d^2 x}{dt^2} = -f + F - kx, \quad (19)$$

where $m$ is the mass of the oscillator and $k$ is the spring constant. Eq. 19 is actually a simple application of Newton’s Law. Since $f$ is the damping force and is proportional to the speed,

$$f = c \frac{dx}{dt}, \quad (20)$$

taking into Eq. (19), we get
Fig. 3.5. An oscillator under three forces.

\[
m \frac{d^2 x}{dt^2} + c \frac{dx}{dt} + kx = F \cdot
\]

(21).

Assuming the vibrating source

\[
F = F(t) = F_0 e^{i \omega t},
\]

(22)

where \( \omega \) is the frequency of the source,

the delayed response of the oscillator is

\[
x(t) = A e^{i(\omega t - \phi)},
\]

(23)

where \( \phi \) is the phase delay of the oscillator.

Taking into Eq. (21) and solving the equation, we get

\[
A(\omega) = \frac{F_0 / k}{\sqrt{1 - \left( \frac{\omega}{\omega_r} \right)^2 + \left( \frac{c \omega}{k} \right)^2}}^{1/2},
\]

(24)

\[
\phi = \tan^{-1} \left( \frac{c \omega / k}{1 - \left( \frac{\omega}{\omega_r} \right)^2} \right),
\]

(25)

where \( \omega_r = \sqrt{k/m} \) is the resonant frequency of this oscillator.

For

\[
c = m \omega_r / Q,
\]

(26)
where $c$ corresponds to the dissipation term $\gamma$ [13], we can change Eq. (24)-(25) into

$$
A(\omega) = \frac{F_0/k}{\left[1 - \left(\frac{\omega}{\omega_r}\right)^2\right]^2 + \frac{1}{Q^2}\left(\frac{\omega}{\omega_r}\right)^2}^{1/2},
$$

$$
\varphi = \tan^{-1}\left\{\frac{1}{Q}\frac{\omega}{\omega_r}\frac{\omega}{\omega_r} \left[1 - \left(\frac{\omega}{\omega_r}\right)^2\right] \right\}.
$$

We can plot Eq. (27) and can get a resonant frequency response curve. We now apply the above theory to an EFM probe as shown in Fig.3.6.

Fig. 3.6. An EFM probe operating under the force of a bimorph actuator.
In Fig. 3.6, a cantilever is excited by a bimorph actuator. A laser is reflected on the back surface of the cantilever and collected into a photon sensitive detector (PSD). The frequency shift due to the force $F$ will be sensed by the PSD. Suppose that $z_0$ is the position change from the bimorph actuator and $z$ is the position change from the interaction of the tip and the sample. Assuming that
\begin{align}
    z_0 &= Z_0 + ae^{i\omega t}, \quad (29) \\
    z &= Z + \mu, \quad (30) \\
    F &= F_0(z) + \frac{dF(z)}{dz} \mu, \quad (31)
\end{align}

together with Eq. (21), we get [13]
\begin{equation}
    m \frac{d^2z}{dt^2} + c \frac{dz}{dt} + k(Z + \mu - Z_0 - ae^{i\omega t}) = F_0 + F_1 \mu, \quad (32)
\end{equation}

where $F_1 = \frac{dF(z)}{dz}$. With the equilibrium condition,
\begin{equation}
    F_0(z) = k(Z - Z_0) \quad (33),
\end{equation}
taking Eq. (33) to Eq. (32), we get the final equation
\begin{equation}
    m \frac{d^2z}{dt^2} + c \frac{dz}{dt} + k(\mu - ae^{i\omega t}) = F_1 \mu. \quad (34)
\end{equation}

Solving this equation with
\begin{equation}
    \mu = Ae^{i(\omega t - \varphi)}, \quad (35)
\end{equation}

we get
\begin{equation}
    A(\omega) = \frac{a}{\sqrt{\left(\frac{k'}{k} - \frac{\omega^2}{\omega_r^2}\right)^2 + \frac{1}{Q^2} \frac{\omega^2}{\omega_r^2}}}^{1/2}, \quad (36)
\end{equation}

\begin{equation}
    \varphi = \tan^{-1}\left(\frac{1}{Q} \frac{\omega^2}{\omega_r^2} - \frac{\omega}{\omega \omega_0 - \omega_0}\right), \quad (37)
\end{equation}

where
\begin{align}
    \omega_r &= \sqrt{k'/m}, \quad \text{and} \\
    k' &= k - F_1. \quad (38)
\end{align}
Taking (39) into (38), we get the approximation at the resonant frequency
\[ \omega_r = \sqrt{\frac{k - F_1}{m}} \approx \sqrt{\frac{k}{m}} \left( 1 - \frac{F_1}{2k} \right). \]  

(40)

With \( \omega_r = \sqrt{\frac{k}{m}} \), we get
\[ \Delta \omega \approx \frac{1}{2 \omega_r} \frac{F_1}{k}. \]  

(41)

Thus working at the resonant frequency, the phase shift is proportional to the force gradient. So in the parallel capacitor model, Eq. (13) can be
\[ F' = \varepsilon_r \varepsilon_0 \frac{S}{Z^2} V^2. \]  

(42)

\( F' \) is more sensitive than \( F \) because it is proportional to \( Z^{-3} \) while \( F \) is proportional to \( Z^{-2} \). Also Eq. (11) is
\[ F' = F_\text{tip}' + F_\text{cone}' + F_\text{cantilever}', \]  

(43)

where \( F_\text{tip}' = \frac{1}{2} \frac{\partial^2 C_\text{tip}}{\partial Z^2} V^2 \), \( F_\text{cone}' = \frac{1}{2} \frac{\partial^2 C_\text{cone}}{\partial Z^2} V^2 \), \( F_\text{cantilever}' = \frac{1}{2} \frac{\partial^2 C_\text{cantilever}}{\partial Z^2} V^2 \).

These second derivatives greatly reduce the force contributions of the cantilever and the cone.

### 3.4 Kelvin probe force microscopy

Kelvin probe force microscopy, with other names of surface potential microscopy, Kelvin force microscopy or even Kelvin probe microscopy, is an extension of EFM. During the process of scanning, a voltage is applied to the tip. If an equal potential is reached, the force between the tip and the sample will be zero. Recording the applied voltages at all points across the sample, we obtain a surface potential image. Supposing the voltage applied on the tip is
\[ V_\text{tip} = V_\text{dc} + V_\text{ac} \sin(\omega t). \]  

(44)

With Eq. (9), we get
\[ F = \frac{1}{2} \frac{\partial C}{\partial Z} \left( V_{\text{tip}} - V_{\text{sample}} \right)^2 \]

\[ = \frac{1}{2} \frac{\partial C}{\partial Z} \left[ \left( V_{\text{dc}} - V_{\text{sample}} \right)^2 - 2V_{\text{ac}} \left( V_{\text{dc}} - V_{\text{sample}} \right) \sin(\omega t) + \frac{1}{2} V_{\text{ac}}^2 \left( 1 + \cos(2\omega t) \right) \right] \]  

(45)

The force consists of three components,

\[ F_{\text{dc}} = \frac{1}{2} \frac{\partial C}{\partial Z} \left[ \left( V_{\text{dc}} - V_{\text{sample}} \right)^2 + \frac{1}{2} V_{\text{ac}}^2 \right], \]

\[ F_{\omega} = \frac{1}{2} \frac{\partial C}{\partial Z} \left[ -2V_{\text{ac}} \left( V_{\text{dc}} - V_{\text{sample}} \right) \sin(\omega t) \right], \]

\[ F_{2\omega} = \frac{1}{2} \frac{\partial C}{\partial Z} \left( \frac{1}{2} V_{\text{ac}}^2 \right) \cos(2\omega t). \]  

(46)

We are interested in the component of \( F_{\omega} \) because \( F_{\omega} = 0 \) when \( V_{\text{dc}} = V_{\text{sample}} \). We use a lock-in amplifier to get \( F_{\omega} \) and obtain the sample voltage when \( F_{\omega} = 0 \). For the tip working at the resonant frequency of the cantilever, i.e. \( \omega = \omega_r \), we get the force gradient,

\[ F_{\omega} = \frac{1}{2} \frac{\partial^2 C}{\partial Z^2} \left[ -2V_{\text{ac}} \left( V_{\text{dc}} - V_{\text{sample}} \right) \sin(\omega t) \right]. \]  

(47)

The total capacitance comes from the tip, the cone, and the cantilever. For the force gradient detection, the influence of the tip is dominant. Eq. (47) can be changed to

\[ F_{\omega}' = \frac{1}{2} \frac{\partial^2 C_{\text{tip}}}{\partial Z^2} \left[ -2V_{\text{ac}} \left( V_{\text{dc}} - V_{\text{sample}} \right) \sin(\omega t) \right]. \]  

(48)

The detection with the force gradient instead of the force greatly improves the lateral resolution of KPM.

### 3.5 Surface contrast transfer mechanism

The measured quantities are not exactly the same as the actual surface potentials or electric fields. The observed potential is the weighted average potential on the sample around the tip \([7, 14]\). Almost all EFM tip-sample models take the sample as an infinitely flat surface. That is not true. In Fig.3.7, regions \( A, B \) and \( C \) are charged areas with corresponding potentials \( V_1, V_2 \) and \( V_3 \).
The electrostatic energy for this system is

\[
W_e = \frac{1}{2} \left[ C_{12} (V_1 - V_2)^2 + C_{13} (V_1 - V_3)^2 + C_{23} (V_2 - V_3)^2 \right] + \\
\frac{1}{2} \left[ C_{1i} (V_1 - V_{tip})^2 + C_{2i} (V_2 - V_{tip})^2 + C_{3i} (V_3 - V_{tip})^2 \right],
\]  

(49)

where \( V_{tip} \) is the voltage on the tip, \( C_{ij} \) is the capacitance between region \( i \) and region \( j \), where \( i \) or \( j \) here can be 1 or 2 or 3 while \( i \) is not equal to \( j \); \( C_{it} \) is the capacitance between region \( i \) and the tip, where \( i \) here can be 1 or 2 or 3 while \( i \) is not equal to \( j \).

The first component of Eq. (49) in brackets is the mutual capacitances between areas. The second component is the capacitances between the areas and the tip. The force gradient between the tip and the sample is

\[
F' = \frac{1}{2} \frac{\partial^2 W_e}{\partial Z^2}.
\]  

(50)

We consider the force gradient only from the tip because the influence from the cone and the cantilever is negligible after the filtering of the second derivatives. The first component of Eq. (49) has no \( Z \) direction variable because three areas lie on the same plane and so its \( Z \) derivative is zero. The equation for the force gradient can be reduced to a simple form,

\[
F' = \frac{1}{2} \left[ \frac{\partial^2 C_{1i}}{\partial Z^2} (V_1 - V_i)^2 + \frac{\partial^2 C_{2i}}{\partial Z^2} (V_2 - V_i)^2 + \frac{\partial^2 C_{3i}}{\partial Z^2} (V_3 - V_i)^2 \right].
\]  

(51)
Fig. 3. Three charged areas are A, B, C, with the capacitance with the tip, $C_{1t}$, $C_{2t}$, $C_{3t}$.

With the same method shown in Eq. (44)-(48), the force gradient at the resonant frequency is

$$F_{\omega} = V_{dc} \left[ \frac{\partial^2 C_{1t}}{\partial Z^2} (V_1 - V_{dc}) + \frac{\partial^2 C_{2t}}{\partial Z^2} (V_2 - V_{dc}) + \frac{\partial^2 C_{3t}}{\partial Z^2} (V_3 - V_{dc}) \right] \sin(\omega t). \quad (52)$$

Finally, while $F_{\omega} = 0$ we get the measured voltage

$$V_{dc} = \frac{\frac{\partial^2 C_{1t}}{\partial Z^2} V_1 + \frac{\partial^2 C_{2t}}{\partial Z^2} V_2 + \frac{\partial^2 C_{3t}}{\partial Z^2} V_3}{\frac{\partial^2 C_{1t}}{\partial Z^2} + \frac{\partial^2 C_{2t}}{\partial Z^2} + \frac{\partial^2 C_{3t}}{\partial Z^2}}. \quad (53)$$

Eq. (53) shows clearly that the measured voltage is a weighted average over the areas around the tip. If one area is sufficiently large under the tip, it can be regarded as an infinite plane and the potential sensed by the tip is almost the same as the actual surface potential. Eq. (53) can be extended to the continuous form if there are many such charged areas that form the continuous voltage distribution. Here, a contrast transfer function $T$ can be introduced as

$$V_{dc} = \vec{V} \cdot T,$$

where $\vec{V} = [V_1, V_2, V_3, \ldots, V_n]$ and
\[ T = \frac{1}{\sum_{i=1} \frac{\partial^2 C_{ij}}{\partial Z^2}} \left[ \frac{\partial^2 C_{1j}}{\partial Z^2}, \frac{\partial^2 C_{2j}}{\partial Z^2}, \frac{\partial^2 C_{3j}}{\partial Z^2}, \ldots, \frac{\partial^2 C_{nj}}{\partial Z^2} \right] \].

For a continuous form,
\[ V_{dc}(x_0, y_0) = \int S V(x, y) T(x-x_0, y-y_0) dx dy, \quad (55) \]
where \((x_0, y_0)\) is the tip location,
\[ T(x-x_0, y-y_0) = \lim_{\Delta x, \Delta y \to 0} \left( \frac{\partial^2 C(x-x_0, y-y_0)}{\partial Z^2} \int_S \frac{\partial^2 C(x-x_0, y-y_0)}{\partial Z^2} dS \right) \cdot (56) \]

The transfer function includes the information of the tip geometry and the sample topography. To get better lateral resolution, the tip has to be as close as possible to the sample without crashing itself on the sample. A blunt tip can improve the lateral resolution [7] because it can make the tip-sample interaction dominant since a blunt tip couples well with the sample.

### 3.6 Single electron detection and high-speed detection

Even if molecular QCAs could operate at the room temperature, we would have to find single electron detectors that can work at the room temperature. EFM can be such a detector. There is capacitive coupling between the tip and the molecule on the sample. This coupling makes charge state detection possible. It has been reported that EFM can detect single-electron motion in a nanotube [15]. The nanotube has double quantum dots.

According to Coulomb’ law, the EFM tip will feel a strong electric field if we bring the tip close to the charge. This large electric force will shift the cantilever resonant frequency. The charge is then detected indirectly by the frequency shift. With this detection method, single charge motion has been observed [16].
We can deposit charges on a sample surface either by corona discharging [17] or by contact electrifying [18]. However they usually deposit more than one thousand electrons. By the introduction of Co nanoclusters [19] or silicon quantum dots [20], both embedded in SiO$_2$, electrons can tunnel from the EFM tip to Co or Si islands. The size of those islands is below 10 nm. The number of the trapped electrons on those islands can be down to 5 to 20 [19]. For single electron tunneling detection, it has been observed only in high vacuum [21-23]. Single electron tunneling occurs only when the gap between the tip and the sample is below 2.5 nm and also there are available empty electron states on the surface [23]. The oscillating amplitude of the tip decreases when electrons tunnel from tip to the dot on the sample. This amplitude difference can be used for the detection of electron tunneling.

High-speed electric field measurement is necessary if we want to investigate the dynamic clocked nanowires. “Dynamic” means that high-frequency signals are applied to clock the nanowires. Our current EFM is operating at only several hertz. Thus we have to either improve the speed of EFM hardware, for instance, increasing the high resolution oscillator frequency and working frequency of the servo controller [25], or adopt a new measurement method [24] to get high-frequency signals from clocked nanowires. The new method boasts of the ability to measure up to 200 gigahertz. With this method, the detection of 3.2 gigahertz IC voltage signals has been demonstrated [26].

For the experimental setup of this method, there are two specific frequencies: one is applied to the nanowire and the other is applied to the tip. The EFM force is modulated by the frequency difference between those two frequencies. The mathematical deduction is as the following. Assume a parallel-plate capacitor as the tip-sample model. According to Eq. (43), the force gradient is

$$ F' = \varepsilon,\varepsilon_0 \frac{S}{Z^3} \nu^2 = \varepsilon,\varepsilon_0 \frac{S}{Z^3} \left( v_{tip} - v_{wire} \right)^2. \quad (57) $$

Assuming initial phases for $\omega_{tip}$ and $\omega_{wire}$ are zero,
\[ v_{\text{tip}} = V_{\text{tip}} \sin(\omega_{\text{tip}} t) \quad \text{and} \quad v_{\text{wire}} = V_{\text{wire}} \sin(\omega_{\text{wire}} t). \]  \tag{58}

Taking (58) into (57), we get
\[ F' = \varepsilon_r \varepsilon_0 \frac{S}{Z^3} \left( V_{\text{tip}}^2 \sin^2(\omega_{\text{tip}} t) + V_{\text{wire}}^2 \sin^2(\omega_{\text{wire}} t)^2 - 2V_{\text{wire}} V_{\text{tip}} \sin(\omega_{\text{wire}} t)\sin(\omega_{\text{tip}} t) \right). \tag{59} \]

After low-pass filtering, the final equation is
\[ F' = \varepsilon_r \varepsilon_0 \frac{S}{Z^3} \left( \frac{1}{2} V_{\text{tip}}^2 + \frac{1}{2} V_{\text{wire}}^2 - V_{\text{wire}} V_{\text{tip}} \cos(\omega_{\text{wire}} t - \omega_{\text{tip}} t) \right). \] \tag{60}

We can use a lock-in amplifier to get the low frequency of \((\omega_{\text{wire}} - \omega_{\text{tip}})\). Not only can we obtain the distribution of the electric field, but also we can know the other frequency if we know \(\omega_{\text{tip}}\) or \(\omega_{\text{wire}}\).

In summary, we discussed the principles of the force gradient detection of EFM. Also KPFM, an extension of EFM, was introduced. EFM can be used for single-charge detection. Also, we explored high speed detection for EFM measurements. In the next chapter we will present phase-contrast imaging of QCA clocking wires by EFM, simulation of electric field distribution, and power consumption of QCA clocking circuits.
4.1 Electric field measurement setup

Usually, an EFM probe scans over a surface and we get an image of the surface. For our multimode scanning probe microscope (MMSPM) [1], the sample stage rather than the probe scans. The sample stage is driven by a scanner tube. Thus, the wires attached to the sample have to move with the stage, which results in a nonlinear force exerting on the stage. Since EFM anticipates the next movement according to the previous feedback, but the nonlinear force is not considered into the feedback, the tip of the probe can crash on the sample in the next movement. To prevent the damage, we have to use wires as thin as possible. After many trials, thin wires below 28 AWG have worked without any problem so far.

The 20-pin substrate with nanowires is soldered into the 20-pin package [2] by wire bonding. The package is then glued onto the metal puck. The metal puck is the sample holder. It can stick to the sample stage on the scanner of the MMSPM. A 10 $M\Omega$ resistor is connected to the nanowire in series to prevent possible melting-down by short-circuit current. So far we have tested two-phase clocked nanowires. The EFM measurement setup is shown in Fig. 4.1.

The clocking signals in Fig. 4.1 are
\[ v_1 = V \cos(\omega t + \phi_1), \quad v_2 = V \cos(\omega t + \phi_2) \] and \[ v_3 = V \cos(\omega t + \phi_3), \] where \( \phi_1, \phi_2 \) and \( \phi_3 \) are different phases.
Fig. 4.1. The setup of EFM measurement of clocked nanowires. The nanowires connect to substrate pads. The wire bonds connect substrate pads to package pads.

The electric field around clocked nanowires shifts the cantilever’s resonant frequency. The photon sensitive detector (PSD) picks up the laser signal reflected from the cantilever and anticipate a frequency shift. This frequency shift is related to the electric field. The electric field intensity is proportional to the voltage difference between the tip and the sample. We can apply voltages to the tip to increase the electric field.
4.2 Electron beam lithography

Electron beam lithography (EBL) has become a conventional tool for nanofabrication. In our laboratory, we have three EBL systems: the Amray, the Hitachi, and the recently purchased Elionix EBL systems. The Elionix EBL system can produce sub-10 nm feature as shown in Chapter 1. The mix-and-match capability of Elionix is still under investigation. The results shown in this section were performed on the other two EBL systems before the installation of Elionix. In this section, we tested the capability of EBL alignment in Amray and obtained extremely fine patterns by using the Hitachi EBL. A possible combination of the Amray EBL and the Hitachi EBL systems is discussed below.

4.2.1 EBL alignment

Compared with the optical lithography, EBL has better resolution and does not need masks. Usually we need one exposure to make our nano devices and connect them to the outside pads that are defined by the optical lithography. Alignment marks are used to align the nano devices to the outside pads. As shown in Fig. 4.2, four gold squares on the center of the substrate act as alignment marks. Those four squares, other wires, and pads are made by optical lithography.

We spin polymethyl methacrylate (PMMA) onto the substrate and bake it on a hot plate at 180 degrees for 5 minutes. The substrate is then loaded into the chamber of the Amray SEM. We use translation and rotation knobs to align the Cartesian axes of this substrate to the axes of the SEM sample stage. We can bring the area that is ready for exposure to the center of scanning field of the electron beam.

Then we use the Nanometer Pattern Generator System (NPGS) software [3] to control the beam. It only opens the four small windows around the four gold squares.
Fig. 4.2. 20-pad substrate made by the optical lithography [3]. There are four alignment squares around the open area in the middle of this picture. The size of the square is about $6\mu m \times 6\mu m$. The size of the open area is about $70\mu m \times 70\mu m$.

So, the area that is ready for exposure is not be exposed during the alignment process. We move four electronic alignment marks on the computer screen to match these gold squares. The software calculates the transformation matrix from the pattern created in the computer to the pattern that actually is exposed on the sample.

We wish to fabricate multi-phase clocked nanowires that can support many parallel computations. The use of multiple levels of interconnects becomes necessary to save the number of pins. Without a multiple-level structure, the 20-pin substrate only supports only about 5 cycles of 4-phase clocking signal. Thus we are concerned with the overlay accuracy. It is necessary to investigate the alignment capability of the Amray EBL system.

We reduce the size of the alignment marks to $2\mu m \times 2\mu m$. These four new gold marks are made by EBL and are placed at the corners of a $40\mu m \times 40\mu m$ area. The backscattered electron (BSE) detector is chosen for the alignment process instead of the secondary electron (SE) detector. The backscattered electrons can penetrate the PMMA layer and obtain high contrast imaging better than SE. The marks with the size below $2\mu m \times 2\mu m$ are hard to see with the BSE detector.
As shown in Fig. 4.3 a Vernier scale is specially designed for overlay accuracy measurement. There are 10 nm differences between the two sets of gratings. Using this gauge is very clear and straightforward. We used the SEM measurement tool to test this Vernier scale. The gap of gratings can be further reduced if the overlay accuracy capability is improved. Mostly the alignment deviations are different in different directions. We designed horizontal and vertical Vernier scales in pairs. These gauges are placed all over the open area as shown in Fig. 4.2. By statistical methods we can obtain the average and the standard deviation.

The process for overlay accuracy measurement is done in two steps. First, the upper half of the Vernier scale (as shown in Fig. 4.3 (a)) and the left half (as shown in Fig. 4.3 (b)) are exposed. Next, the wafer is reloaded into the SEM and the other halves are exposed. After developing the exposed patterns we sputter 2 nm gold coatings and do SEM imaging of the PMMA surface instead of metal after lift-off.

We do not develop the first half pattern until the whole pattern is developed under the same conditions. We cannot use metal wires after lift-off for our overlay accuracy measurement because it might introduce new error due to shadow evaporation. The final result for $2\mu m \times 2\mu m$ alignment marks is shown in Fig. 4.4. The deviation maybe is due to the mechanical relaxation of translation knobs or the electronic shifting of the electron beam.
Fig. 4.3. Horizontal and vertical Vernier scales designed for displacement gauge. (a) 30 nm displacement rightwards. (b) 30 nm displacement upwards.
Fig. 4.4. Data collected for 35 samples with 5 double-EBLs at 7 different locations. (a) Horizontal deviation map. (b) Vertical deviation map.
4.2.2 Mix-and-match method for EBL

There are two EBL systems converted from conventional SEMs by Dr. Bernstein’s group: one is the Amray EBL system and the other is the Hitachi EBL system. The Hitachi EBL system was built by Wenchuang Hu [5]. The software for Hitachi EBL is V5 developed by Bazan [6]. The Hitachi EBL can achieve about 10 nm metal wires [5], which is very hard to achieve with the Amray EBL. Electrons extracted from the cold field-emission tip in the Hitachi form a smaller beam than that of electrons emitted from the hot tungsten filament in the Amray. However, the Hitachi EBL system has not implemented its alignment function so far. The alignment capability is critical because we have to connect nano devices out and test these devices with external signals. Multiple levels of interconnects also need this capability.

The functions of the two EBL systems can be combined. We can make nano devices in the Hitachi and record their relative location to the alignment mark that is used for alignment in the Amray. This method has been used extensively for those devices that cannot be fabricated by the top-down scheme, for instance, self-assembly molecules such as carbon nanotubes [7]. It is difficult to place a carbon nanotube at a specific location [8]. However, using this method we can pick up one carbon nanotube from the sample surface where many nanotubes grow. The relative location to the alignment mark is used to make conductive metal wires [7]. We can call this strategy “mix-and-match” because there are two lithography systems, although the “mix-and-match” is usually used for the connection between optical lithography and EBL [9-11].

The alignment capability of the Amray EBL has been shown at the beginning of this chapter. For the Hitachi EBL, recent results are shown in Fig. 4.5. 1.2% 950 K PMMA was spun at 4000 RPM for a thickness of around 50 nm. The sample was baked on a hot plate at 200 °C for 4 min. The acceleration voltage was 30 kV with the probe current at 15 pA and working distance at 9 mm. After exposure, the sample was
developed in MIBK: IPA: MEK=1:3:1.5% solution for 40 seconds [5] and 1.5 nm Platinum was sputtered on the sample surface for SEM imaging. As shown in Fig. 4.5 (b), sub 10 nm PMMA trenches were achieved. There are discontinuities along some lines in Fig. 4.5 (a). These discontinuities could cause open circuits after metal deposition and lift-off. The problem can possibly be solved by decreasing the beam stitching step or the “cold” develop method invented by Hu et al. [5] in which the PMMA on the sample is developed below room temperature. The method can yield uniform and even narrower PMMA trenches.

![Fig. 4.5. SEM pictures of PMMA surface with 1.5 nm Platinum coatings after develop. (a) 16 nm nanowires. The scale bar is 200 nm. The line dose is 0.8 nC/cm. (b) Sub 10 nm nanowires. The scale bar is 100 nm. The line doses from the top are 0.3, 0.4 and 0.2 nC/cm respectively.](image)

The metal lift-off now becomes our concern. The SEM pictures show only the top surface of PMMA. We do not know whether there is some residue at the bottom of those trenches. The residue is mostly due to under-developed PMMA. With the residue at the bottom, the metal after deposition will get lifted away. During the develop process, using ultrasonic excitation can increase the possibility of washing out the residue [12-13]. As shown in Fig. 4.6, a nanowire was made by ultrasonically assisted
develop in the solution of MIBK: IPA: MEK=1:3:1.5% for 20 seconds and metal deposition. It is possible to combine the ultrasonic and “cold” development methods to fabricate extremely narrow nanowires.

4.3 Electric force microscopy

Electric force microscopy (EFM) is used to measure the electric field emitted by clocked nanowires. Here, we propose a device navigation map for EFM and present recent EFM imaging results.

4.3.1 Device navigation map for electric force microscopy

A type “J” scanner is used in our EFM imaging. For this scanner the scanning area is $125 \mu m \times 125 \mu m$. The size of our clocked nanowires is at the micron level. Instead of painstakingly looking around the whole field, we can use a navigation map as shown in Fig. 4.7 to find the exact location of the nanowires in a few steps. Each square in Fig. 4.7 has a small square inside.
The relative location of the small square to the outside square is corresponding to the location of current scanning region to the whole sample area. It is unnecessary to scan all over the field to search for the nanowires. A few steps’ searching can increase the life time of an EFM probe by saving unnecessary scanning.

The navigation map is important to our future molecular QCA test devices. The final clocked nanowires will be passivated and planarized with a layer of silicon dioxide. A flat surface is obtained after chemical mechanical polishing (CMP) or spinning some liquid dielectrics. The flat surface is good to deposit molecules. We can still use the map to find our pattern. We can apply voltages to the buried navigation pattern. This electrical pattern can be detected by EFM. This pattern will be exposed with the pattern of nanowires in the same EBL. Shapes of outside squares are defined by line doses of electron beam. The inside squares can be exposed with area doses to improve the contrast. An instance of the geometrical navigation is shown in Fig. 4.8.
4.3.2 EFM imaging results and interpretation

950 k molecular weight PMMA with a concentration of 1.2% in chlorobenzene is spun on the 20-pad substrate at 4000 rotations per minute (RPM) for 30 seconds. After baking on a hot plate at 180 degrees for 5 minutes, the sample is ready for EBL. We use 4.2 nC/cm line doses for nanowires. The pattern is developed in MIBK: IPA: MEK=1:3:1.5% solution for 40 seconds [14]. 5 nm Ti and 35 nm Au are deposited. After lift-off in acetone for 1 hour we get metal wires. As shown in Fig. 4.1, the wires connect to the substrate pads directly. Wire-bonding connects the substrate pads to the package pads. 28 AWG wires connect package pads to external measurement circuits.

The SEM imaging of clocked nanowires is shown in Fig. 4.9 (a) and the corresponding AFM picture is shown in Fig. 4.9 (b). The size of nanowires in the AFM picture, about 100 nm, is bigger than that in SEM picture, about 80 nm. That is caused by the tip’s open angle. When the tip is scanning on a rough sample surface, due to this open angle it cannot follow the curve of edges. Smaller tips results in higher lateral resolution.
We can apply different voltages to nanowires to simulate multi-phase clocking signals at a particular time. For instance, 10 volts and ground can be regarded as 90 degree phase difference for a time-variable voltage signal. In the future, we can use the method described in Chapter 3 to measure high speed circuits. Figure 4.9 (c) shows EFM imaging of two-phase clocking signal. 10 volts and grounded nanowires are alternated.

The EFM tip can be biased at different voltages. Increasing the voltage difference between tip and nanowire can enhance the phase contrast. In Fig. 4.9 (c), the initial phase at the start of scanning is at about 2 degrees. The resonant frequency of the cantilever decreases when the tip is attracted by the electric force. Then the phase delay occurs. We can use sharp probes to get high lateral resolution. As shown in Fig. 4.10 (a), compared with a tip with the diameter around 30 nm, a sharp tip with the diameter around 15 nm has better resolution in AFM imaging. However, as shown in Fig. 4.10 (b), the lateral resolution for EFM imaging is not greatly improved for the sharp tip.
Fig. 4.9. Different images of same clocked nanowires. (a) The distance between wires is 400 nm as shown in the SEM pictures. (b) AFM imaging in tapping mode where electric field cannot be detected. (c) Two-phase electric field is detected by EFM. The bright line is applied with a positive voltage and the other is grounded. The EFM tip is grounded and the lift height is 30 nm.
Fig. 4.10. AFM and EFM pictures of the same circuits with different tip sizes. (a) The inset pictures show SEM pictures of two tips pointing to AFM pictures respectively. The diameter of the upper tip is 30 nm and the diameter of the other tip is 15 nm. (b) Corresponding EFM pictures. The distance between wires is 200 nm. Lift height is 63 nm. 4 volts is applied with alternate ground wires.
In AFM tapping-mode, the tip is very close to the surface, while in EFM lift-mode we place the tip at 63 nm from the surface. Below this distance, the tip can be easily crashed on the rough surface. The advantage of a sharp tip cannot be exploited for current lift heights. The lift height can be a few nanometers for a flat surface. The improvement in EFM imaging with a sharp tip will be demonstrated in our coming devices. We can apply PMMA or chemical vapor deposition (CVD) SiO2 to get a flat surface so that we can lower the lift height to improve the lateral resolution. In the future, we can hopefully grow a carbon nanotube on the tip. Carbon nanotube tips have been demonstrated for improving the lateral resolution [15].

To change the electric field intensity, we either vary the lift heights as shown in Fig. 4.11 (a) or change the voltages applied to the nanowires as shown in Fig. 4.11 (b). With the voltage increasing, the intensity of electric field increases too. The lower the lift height results in higher intensities of electric fields.
Fig. 4.11. EFM pictures at different lift-heights and different voltages. (a) The top is AFM picture for the topography. The distance between wires is 200 nm. The other three are EFM pictures with lift-heights at 63 nm, 126 nm and 199 nm. The voltages applied are 14 volts and ground. (b) The first one is AFM picture for the horizontal direction scanning. The vertical direction is disabled. The distance between wires is 400 nm. The second one is EFM picture with different voltages. From the top, there are 2.6 volts, 1.4 volts, ground and 3.6 volts. The lift height is at 40 nm. Dark lines are negatively charged.
There is a streak when the applied voltage is changed from ground to 3.6 volts. The streak always occurs when we change the voltages abruptly. It is perhaps due to the function of circuit protection in the case of a sudden increase in force. The feedback circuit may compensate the sudden force for a reverse phase contrast. The phenomenon looks as if charges accumulate on the tip instantaneously. For the cross-section analysis of Fig. 4.11 (b), we get Fig. 4.12.

Fig. 4.12. The cross-section analysis of Fig. 4.11 (b). Red curve represents 3.6 V signal while green curve represents 2.6 V signal. Dotted blue curve shows the corresponding topography by AFM imaging.
In Fig. 4.13 (b), the blue curve is for the topography and the red curve is for the EFM imaging. Just above the nanowires, there are no peaks or valleys. The maximum and the minimum electric fields lie between nanowires. We have a simple explanation for this result. When the distance between clocked wires decreases, the electric force between wires becomes dominant.

In Fig. 4.13, the distance between nanowires is 200 nm while in Fig. 4.12 the distance between nanowires is 400 nm. For 200 nm spaced nanowires, the electric field intensity between nanowires is nearly doubled. Before the EFM tip starts scanning, charges have already accumulated on the nanowires. When the tip dips into trenches between nanowires, it feels a strong force. The force bends the cantilever. An angle is formed between the cantilever and the surface. Thus the force has a component vertical to the cantilever. The component shifts the resonant frequency of the cantilever. The direction of the component changes with the direction of the electric field between nanowires. Even in 400 nm spacing nanowires, when the voltage applied is increased to a certain point, we can still get small peaks of electric field inside the trenches.

Further investigation of this interesting phenomenon could be done by adding a PMMA layer over the nanowires and measuring electric fields emitted from the nanowires with the PMMA layer covered. If the peaks or valleys are still there, the simple explanation would be not right because the tip cannot dip into the trenches and the force is not coming from the trenches. We would have to explore new explanations.
Fig. 4.13. EFM imaging of clocking circuits with 200 nm distance between wires. 3.3 V is applied and the lift-height is 63 nm. (a) Topography imaging above and corresponding EFM imaging below. Both two parts show the cross-section lines. (b) Cross-section lines in (a) for the two parts. The solid curve is for EFM imaging and dotted blue curve is for topography.
As shown in Fig. 4.14 we have observed a charging effect. The charging effect may be due to corona discharging or contact electrifying [16-18]. In our sample, the metal for nanowires is gold. Some PMMA residue or other organic dirt is on the surface of the nanowire. They can act as the clusters for trapping electrons. When a high electric field is applied and the tip scans above the nanowire, charges might tunnel into those clusters and accumulate there. When the voltage is withdrawn, the charges disappear slowly like the discharging of a capacitor. In Fig. 4.14 we disable the slow scan axis, i.e. Y axis. Thus, the Y axis records each scan across the same area and acts as the time axis since we know the scan speed. The cause of the streak in Fig. 4.14 (a) may be due to the circuit’s protection for a sudden voltage change.

We are also interested in the mutual interference between the AFM imaging and the EFM imaging [19]. The mutual interference is also called cross-talking. During the process of AFM imaging, the tip feels not only the contact force from the surface, but also a long range electric force emitted from nanowires. The electric force might influence the geometrical imaging. Our recent results have proven this cross-talking, which will be discussed in Chapter 5.
Fig. 4.14. The charging effect of 400 nm inter-distance nanowires. The lift height is 20 nm. The Y direction is disabled. The whole process is about 4.6 minutes. At t1 = 0.6 minute, the 7.4 volts voltage is withdrawn. t2, t3, t4 and t5 are at 1.6, 2.6, 3.6, and 4.6 minutes respectively. (a) The topography by AFM in tapping-mode. The second is EFM imaging. (b) The time evolution of discharging. All these time points are not in the region of the streak.
4.4 EFM tip as a point on a grounded plane

According to the clocking scheme presented by Lent et al. [20, 21], a ground metal layer above the clocked nanowires directs electric field upward. If such a layer is added, it is impossible to detect the electric field with EFM. Without this layer, the electric field energy concentrates between wires, not above the wires. This electric field is not the same as that with the ground metal layer. The electric field detected by EFM is different from the actual electric field without EFM tip introduced. Fig. 4.15 shows the simulation results by Maxwell 2D software [22].

In Fig. 4.15, we can see that the electric field detected by EFM in (b) is not the actual electric field in (a). Fortunately, since the EFM tip is grounded, it can be regarded as a ground point. Thus the electric field detected at that point is just like that with metal ground layer if the tip is sharp and close to the surface. If we have a flat surface above the nanowires, the whole area that the tip scans over can be regarded as a grounded metal plate. For a coarse surface, we cannot bring the tip too close to the nanowire.
Fig. 4.15. Maxwell 2D simulations of electric field distributions with or without EFM tip. (a) Without EFM tip. (b) With the EFM tip introduced 15 nm above the middle wire. Nanowires are 10 nm high and 10 nm wide. The distance between wires is 20 nm. 1 volt is applied to the middle wire and the other two are ground. EFM tip is grounded.
For future work, silicon dioxide or PMMA can be used for a planarization layer above clocking nanowires. Kelvin probe microscopy (KPM) will be exploited to obtain the absolute values of surface potentials. With the planarization layer, we will test the minimum voltage sensitivity of KPM to check whether it can detect the potential change in a redox molecule when electrons hop from one dot to another. Also we will test the lateral resolution of EFM with our extremely narrow nanowires and CNT probes.

In summary, the electric fields emitted from QCA clocking wires have been detected by EFM qualitatively. Also, we investigated the alignment capability of EBL system. The EFM tip as a point on a ground plane was discussed. In the next chapter we investigate a source of error in EFM measurements that must be taken into account for quantitative measurements.
CHAPTER 5
APPARENT HEIGHT IN TAPPING MODE OF ELECTROSTATIC FORCE
MICROSCOPY

We investigate a source of error in electrostatic force microscopy (EFM) measurements. During EFM, the probe performs two scans: the first to obtain the topography in tapping mode and the second at a chosen lift height to measure the electrostatic force. However, during the first scan, the electrostatic force between the probe and sample can cause error in the height measurement. In this work, micron-sized wires are fabricated, and test voltages applied. Experiments demonstrate that attractive electrostatic forces result in erroneous height measurements. A tip-sample interaction model is provided, and simulation results are in good agreement with experimental data.

5.1 Introduction

Since the advent of atomic force microscopy (AFM), many variations have emerged depending on the source of the interaction force, for example, magnetic force microscopy that detects the force due to dipole interactions between magnetic domains and a magnetized tip [1], chemical force microscopy that probes forces between different molecular groups [2], and electrostatic force microscopy (EFM) that measures long-range electrostatic force [3]. EFM has many materials-related applications including measuring the surface potential or contact potential [4-5], detecting charges on surfaces or nanocrystals embedded in an SiO₂ matrix [1,6-11], and probing surface dopant
profiles on silicon [12]. During EFM probe scanning, the cantilever oscillates at its resonant frequency. The phase and frequency shifts of the cantilever are proportional to the electrostatic force gradient. Most force gradient comes from the tip of the probe since the electrostatic influences from the cone and cantilever drop off quickly with distance. Thus, the lateral resolution is enhanced [13-14] compared with Kelvin probe force microscopy [5] (KPFM) (also called surface potential microscopy), an extension of EFM that measures the surface potential by the null-force method.

Scanning for EFM is usually done in two steps. First, the topography is recorded by tapping mode scanning [15]. The tapping mode is also called “intermittent-contact” (IC) mode, contrary to “non-contact” (NC) mode, for which the tip of the probe does not touch the sample surface; while for IC mode, during one period of oscillation, the tip may touch the surface for a very small part of the oscillating cycle. Second, to prevent influences from short-range chemical or mechanical forces from the surface, the probe is lifted parallel to the “topography” at a constant height while scanning, a technique called “lift scanning” or “EFM scanning.” The EFM scanning technique assumes that the influence from short-range forces can be ignored at the lift height, and only the electrostatic force affects the amplitude, frequency or phase of the cantilever.

However, the topography data obtained during the first scan can include information from any electrostatic forces [16], which may be the case for isolated charges embedded in a dielectric layer or on the surface. We have found that in addition to local forces, attractive electrostatic forces contribute to the apparent height, so it turns out that the measured topography in the presence of electrostatic forces can be higher than the actual value. Therefore, we must take this error in apparent height into consideration.
5.2. Methods and experimental results

We used a commercial Veeco MultiMode Scanning Probe Microscope with Nanoscope IV controller for our EFM measurements on patterned metal structures. Micron-sized, gold wires were patterned on 420 nm thick, thermally-grown, silicon dioxide on a silicon substrate by electron beam lithography followed by electron beam metal deposition (Ti/Au=10 nm/40 nm). After lift-off, the substrate was wire-bonded to a package, and connected to voltage sources as shown in Fig. 4.1. The wires were 1μm wide and 20 μm long on a 2 μm pitch. We used EFM probes with conductive platinum-iridium coatings, which are hard and resist oxidization. Our EFM probes exhibited the following characteristics: spring constant of the cantilever \(k_c=0.47 \text{ N/m}\), resonant frequency \(f_r=69.782 \text{ kHz}\), drive frequency \(f_d = 69.771 \text{ kHz}\), and quality factor \(Q=244\). The tapping mode feedback setpoint for the experiment was 1.172 volts, and the drive amplitude was 1.030 volts.

Figure 1 shows the cantilever control mechanism. A voltage-controlled bimorph actuates the cantilever at a frequency close to resonance, and a photosensitive detector (PSD) detects the laser light reflected from the back of the cantilever. The tip side of the cantilever is conductive and is grounded in this experiment. For the tapping mode measurement, the feedback signal is the amplitude of the oscillating cantilever. The distance between the tip of the probe and the sample surface is controlled in order to maintain a constant oscillating amplitude. For our microscope, the sample stage is moved up and down to change the tip-sample distance while the probe is fixed.

The metal wires are energized from -10 to 10 volts. For comparison of tapping mode images, we placed wires at ground and positive and negative voltages side by side. Figure 5.1(a), from the left, shows the topography of five wires: the first and fifth charged at -5 volts, the second and the third grounded, and the fourth at 5 volts. The non-grounded wires appear higher than the grounded wires. Using cross-section
analysis of the middle four wires as shown in Fig. 5.1(b), we can measure the height differences between wires. We see in Fig. 5.1(c), enlarged from the dotted square in Fig. 5.1(b), that the surface of the grounded wire appears rough whereas the surface of the wire with applied voltages appears smooth. The relative smoothness in the +5V wire data is due to two phenomena: First, the electrostatic force causes the probe to lift away from the surface to maintain fixed feedback amplitude, so the long-range electrostatic forces derive from a larger area, thus averaging out surface features. Second, the probe above the non-grounded wire is now working in non-contact (NC) mode, so local forces have less influence on the probe, and fine features disappear.
Fig. 5.1. (a) Topographic image of micron wires by tapping mode. (b) Cross-section analysis of the white line in (a). (c) Enlarged view of the dotted square in (b).
In this section we calculate the apparent height difference observed above for various applied voltages. For our analysis, we must determine under which mode the probe functions, i.e. IC mode or NC mode. In order to reduce the effects of the roughness of the gold surfaces and other noise sources in our experimental data, we compare the average values between the edges of the wires. The result is shown in Fig. 5.2.

![Graph showing height difference between energized and grounded wires as a function of applied voltage. The circles are for positive applied voltages and the triangles are for negative applied voltages.](image)

Fig. 5.2. Height difference between energized and grounded wires as a function of applied voltage. The circles are for positive applied voltages and the triangles are for negative applied voltages.
5.3. Theory and simulation results

5.3.1 Theory about height difference

According to the theory of an oscillating tip-cantilever (OTCL) system [17], the distance between the surface of the sample and the equilibrium rest position of the OTCL for the IC mode can be expressed as,

\[
D_{IC} = A_0 \left\{ 1 - \left( \frac{C}{a} \right)^{3/2} \right\},
\]

with \( C = \left( \frac{3\pi}{4\sqrt{2}} \right) Qd \left( u^2 - 1 \right) + \sqrt{1 - (ua)^2} + \left( Q\kappa_w/6\sqrt{2}d_c^{3/2} \right) \left( 1/\sqrt{a} \right) / Q\kappa_s, \)

\( a = A_0/A_0, \ U = f_d/f_r, \) van der Waals force coefficient \( \kappa_w = Hr/k_c A_0^3, \) \( d_c = d_0/A_0 \) and \( \kappa_s = k_s/k_c, \) where \( k_c, f_r, f_d, \) and \( Q \) were defined above, \( A_0 \) is the amplitude of free oscillation at the resonant frequency \( f_r \), \( A \) is the amplitude of oscillation, \( H \) is the Hamaker constant, \( r \) is the tip radius, \( k_s \) is the sample stiffness, and \( d_c = 0.165 \) nm is the tip contact distance.

The full analytical solution of the height difference by taking Hudlet’s [18] or Colchero’s [19] formulas into the variational principle [17] is very difficult. Instead, for van der Waals plus the additional attractive electrostatic forces, the total OTCL-sample interaction potential can be written as [10]

\[
U_r = U_w + U_E = \frac{1}{D} \left( \frac{Hr}{6} + \frac{\epsilon_0 S^*}{2} V^2 \right),
\]

where \( D \) is the distance between the surface of the sample and the equilibrium rest position of the OTCL, \( S^* \) is the effective tip-sample area for a simple parallel plate capacitor model, \( V \) is the voltage difference between the tip and the sample, and \( \epsilon_0 \) is the vacuum permittivity. The contact potential difference between the probe and the gold wire is negligible here. With Eq. (2), we obtain the distance between the surface of the sample and the equilibrium rest position of the OTCL for the NC case with the additional electrostatic force [10],
\[
D_{NC} = A_0 \sqrt{a^2 + \left( \frac{\kappa_w/3 + 2 \kappa_e V^2}{(1-u^2) + Q^{-1} \sqrt{a^2-u^2}} \right)^{2/3}}, \tag{3}
\]

with electrostatic force coefficient \(\kappa_e = \frac{\varepsilon_0 S^*}{2k_c A_0^2}\).

As shown in Fig. 5.2, the height difference, \(D\), between the grounded wire and the wire with applied voltage can be obtained by subtracting \(D_{IC}\) in Eq. (1) from \(D_{NC}\) in Eq. (3),

\[\Delta D = D_{NC} - D_{IC}.\tag{4}\]

We can see from Eq. (4) that the height difference is a function of the applied voltage. There are two solutions for this function, corresponding to the two branches of Eq. (3).
Fig. 5.3. Comparison between experimental and simulation results from Eq. (4). Data for positive voltage are circles. Data for negative voltage are triangles. Using an effective area of $8S_0$, the simulation data in the solid curve overlaps well with lower part of the experimental data. With an effective area of $18S_0$ the simulation data in the dotted curve roughly fits the higher portion of the experimental data.

5.3.2 Effective area and discussion

With other parameters, $H = 3.75 \times 10^{-19}$ J according to the Lifshitz solution [20], $A_0 = 55 \text{ nm}$, $a = 0.8788$, $u = 0.9998$, $\kappa_w = 3.66 \times 10^{-5}$, $\kappa_c = 2.71 \times 10^{-5}$, $k_i = 78 \text{ N/m}$, $r = 10 \text{ nm}$, $C = 3.41 \times 10^{-4}$, we obtain the simulation results in Fig. 4 for two different effective areas. As explained in ref. [17], the two branches of Eq. 3 refer to a hysteresis effect in the tip/sample distance. Since the hysteresis is a relatively small fraction of the total distance, we plot the average value of the two branches. Assuming $S_0 = \pi r^2$, in Fig. 5.3 the solid curve represent $S^* = 8S_0$, and the dotted curve represents $S^* = 18S_0$. We see in Fig. 5.3 that the experimental data fits the
smaller effective area at lower voltages, and the larger effective area at higher voltages. This shows that the effective tip-sample area increases with increasing applied voltage. A possible explanation for this behavior is offered below.

The total long-range electrostatic force comes from the cantilever, cone, and tip. With the voltage, and therefore distance, between the tip and the sample increasing, the constant-area, parallel-plate capacitor model between the tip apex and the sample is no longer valid. The height difference increases more rapidly with voltage than is predicted by Eq. 4, implying that the effective area of the parallel-plate capacitor model increases as the tip moves away from the surface. As height increases, the capacitance due to the tip decreases rapidly, while the capacitance due to the cone decreases slowly [21]. Therefore, the portion of the total capacitance due to the cone relative to the tip increases with distance, and therefore applied voltage. Since the cone has a larger effective area than the tip, the total effective area of the capacitor increases with increasing height. The effective area of the capacitance as a function of the voltage is shown in Fig. 5.4 with two curves corresponding to the average of the two solutions of Eq. (4), one each of positive and negative applied voltages.
5.3.3 Tip-sample model

The electrostatic force sensed by the probe comes from the cantilever, cone, and tip. In our experiment, alternating parallel wires are energized with positive and negative voltages at the same absolute value. The total effects on the relatively large cantilever from these wires cancel each other and can be ignored. Also, the outside pads on the substrate are millimeters away from the center, and can also be neglected. For most models of EFM tip-sample interaction [10, 18-19, 22], the sample is considered as an infinite surface, which is not true in our case, since the total force is the convolution of the probe and the surface geometry.

We now perform a calculation of the effective area of the probe. As a rough estimate, a coefficient related to the tip-sample distance is multiplied to the force from
the cone. For the force from the tip, the sample surface can be modeled as an infinite surface because the tip is so small compared with the 1 μm wide wire. Thus, we get

\[ F_{\text{total}} = \beta F_{\text{cone}} + F_{\text{apex}}, \quad (5) \]

where \( \beta = \beta(\Delta D) = \frac{W}{2\Delta D \tan(\theta)} \). Here, \( W \) is the width of the wire and \( \theta \) is the half angle formed by the apex of the tip and the radius of the circle of influence of the electrostatic forces from the wire. This cone covers most of the area of the wire from where the electrostatic force originates. \( \beta \) is a function of the tip-sample distance, which is also a function of the applied voltage.

The effective area of the capacitance can be derived from

\[ F_{\text{total}} = \frac{1}{2} \frac{\partial C}{\partial z} V^2 = \frac{1}{2} \frac{\varepsilon_0 S^*}{(\Delta D)^2} V^2, \quad (6) \]

where \( C \) is the total capacitance of the cone plus tip and \( z \) is the vertical direction.

Taking Eq. (5) into Eq. (6), with Colchero’s formulas [19], we obtain the simulation results shown in Fig. 5.5. Figure 5.5 shows the simulated cone and tip influences due to an infinite surface (dashed line), for a 1 μm surface (\( \theta = 89.6 \text{ deg.} \)) (solid line), and the tip alone over an infinite surface (dotted line). (For clarity, only results for positive applied voltages are shown. The results for negative voltages are similar.) The solid curves at \( \theta = 89.6 \text{ deg.} \) agree qualitatively with the experimental data in Fig. 5.4.

Our experiment explains why lift height can sometimes be assigned a negative value for commercial KPFM measurements [23]. Because of the additional height introduced by the electrostatic force during topographic scanning, the lift height for the second scan in KPFM measurements can sometimes be negative, without crashing on the surface, in order to bring the tip closer to the surface for purposes of enhancing the lateral resolution.
Fig. 5.5. Effective probe area for positive voltages simulated with Colchero’s formulas for both finite and infinite sample area. The dashed curve is the tip-sample model including cone and tip with an infinite surface, the solid curve is for the experimental data, and the dotted curve is the tip-sample model considering only the tip.

In summary, we investigated the apparent height introduced by electrostatic force and pointed out the problem of EFM scanning especially for measuring isolated charges on a sample surface. We conclude that the true height should be calibrated to obtain the electrostatic force for quantitative measurements discussed in the next chapter.
CHAPTER 6
A QUANTITATIVE METHOD FOR ELECTROSTATIC FORCE MICROSCOPY-
PHASE MEASUREMENTS

Electrostatic force microscopy (EFM) has become a powerful tool for investigating charges on surfaces. The use of phase measurement in EFM is a direct and fast way to detect electrostatic force gradients, but only qualitatively. With the dual-pass scheme, the phase signal at lifted height is often assumed to exclude any influences from the topography, but it does not. We report the collection of both topography and phase data by EFM on charged, micron-sized metal wires. In order to quantify the electrostatic force, a cone model and finite element analysis are provided to integrate the force gradient from the phase signal.

6.1 Introduction

Electrostatic force microscopy (EFM), an important scanning probe technique, is a variant of atomic force microscopy that detects mostly long-range electrostatic forces [1, 2]. Examples of applications of EFM include the detection of isolated charges in several systems including poly(methyl methacrylate) (PMMA) surfaces [3], charged carbon nanotubes [4], charges inside a silicon dioxide matrix [5-7], and polarization in
ferroelectrics [8-9]. EFM can even detect the electrostatic dipole field of individual molecules [10] and single electron tunneling events [11-13]. In order to ensure conductivity to the tip, EFM probes are usually coated with a thin metal film or are made of highly-doped silicon. The vertical component of the electrostatic force is due to the interaction between the conductive probe and the sample surface by the principal of virtual force [14],

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2,$$

(1)

where $C$ is the capacitance between the probe and the sample, $z$ is distance in the vertical direction, i.e. normal to the sample surface, and $V$ is the voltage difference between the probe and the sample. Many theoretical models [15] have been presented for detailed analysis of the capacitance including the simple parallel-plate capacitor [1], the sphere model [16], the macroscopic cone model [17], and the tip-cone-cantilever model [18-19]. Analytical solutions [20] and finite element analysis methods [21-22] have also been applied.

In order to prevent any influences on the EFM data from the topography, a dual-pass scheme is usually adopted. First, the topography is recorded by tapping mode along a line scan. Next, phase information is recorded along the same line while the probe is lifted parallel to the “topography” at a constant height. This dual-pass technique assumes that the influence from short-range forces can be ignored at the lift height, and only the electrostatic force affects the oscillation amplitude, frequency or phase of the cantilever. However, it turns out that the residual electrostatic force can still influence the topography measurement during the first pass [23-25], and is critical for quantitative measurements, especially for counting electrons [11-13].
While scanning the sample surface, the cantilever vibrates at its resonant frequency. The phase delay is the difference between the phase of the excitation signal for the bimorph actuator and that of the laser signal detected from the cantilever. We define the phase shift, $\Delta \Phi$, as the phase delay away from the resonance of the cantilever, which will be discussed below. This phase shift is proportional to the force gradient [26], so EFM-phase measurements can quickly detect the presence of interaction forces between the tip and sample with high resolution. However, quantitative analysis of the electrostatic force from the phase signal has not been derived [27-28]. Here, we report quantitative force measurements on micron-sized metal patterns used for EFM measurements. The topography and phase signals are obtained by the dual-pass scheme. For quantitative analysis with a cone model, we consider the apparent height due to residual electrostatic force.

6.2 Experimental

Our experiment used a Veeco Multi-Mode scanning probe microscope with a Nanoscope IV controller. Our measurement sample consisted of Ti/Au wires on a 2 $\mu$m pitch, 20 $\mu$m long, 1 $\mu$m wide, and 50 nm high (Ti 10 nm and Au 40 nm). The EFM probe cantilever (Model: Veeco SCM-PIT) exhibited a spring constant of $k=0.48$ N/m, resonant frequency $f_r=70.10582$ kHz, drive frequency $f_d=70.05947$ kHz, and quality factor $Q=254$. The oscillating amplitude was around 50 nm and the stage scan rate was 10 $\mu$m/s. In this instrument, the stage moves up and down to keep the amplitude of the cantilever oscillations constant at its resonant frequency.

In our experiment, the EFM probe is grounded and the micron-sized wires are either grounded or charged to 5 volts. These EFM probes are coated with a
hard platinum-iridium film with good oxidation resistance, and compared with the large applied voltage of 5 volts, the contact potential difference between the gold wires and the platinum-iridium coated probe can be ignored. We chose one-micron sized wires, rather than smaller ones, because the tip of the EFM probe is about 20 nm in diameter, and these wires allow easy data acquisition without distortion from the topography, yet are small enough to obtain the phase and topography comparison in one scan field.

6.3 Results and discussion

Figures 1 (a) and (b) show topography and phase-shift images at the lifted height of 55 nm, respectively, using dual-pass scanning. In Fig. 1 (b), the darker shade of the phase shift corresponds to stronger electric field. The cross-sectional analysis of the lines shown in Fig. 1 (c) erroneously suggests that the energized wire is 8 nm higher than its neighboring ground wires, and also that its surface has an oscillating topography. It has been shown [25] that due to residual electrostatic force, the apparent height of the charged wire varies with the applied voltage. In our data, the wavelike oscillation of topography or phase shift at the charged wire is likely due to the delay time for the stage to adapt to the change of the electrostatic force. The relative smoothness of the topography of the charged wire suggests that during the tapping mode scan, the probe is not affected by local forces such as mechanical and van der Waals forces, but rather only long-range electrostatic forces [25, 29]. Put another way, the tip is in non-contact mode, such that it oscillates about 8 nm above the surface of the charged wire due to the effects of the electric field. The corresponding phase-shift cross-section shown in Fig. 1 (c) suggests that the phase shift for the ground wire is not zero. This experimental offset was taken into account in subsequent calculations.
Fig. 6.1. Topography (a) and corresponding phase imaging (b) of six micron-sized wires; (c) cross-section analysis of the white lines in (a) and (b). In (a), the width of the wire is 1 micron and the distance between wires is 1 micron. In (c), the solid curve represents the phase signal while the dash-dotted curve represents the topography signal.
At the resonance of the cantilever $\omega = \omega_0$, the phase delay is $-\pi/2$ for the case of oscillating freely in air [26]. Away from resonance, the phase shift $\Delta\Phi = \varphi - (-\pi/2)$ is [26]

$$\Delta\Phi \approx -\arctan\left(\frac{Q}{k} F'\right), \quad (2)$$

where $F'$ is the electrostatic force gradient, i.e. the derivative of electrostatic force $F$ with respect to $z$. Taking Eq. (1) into Eq. (2), we get [28]

$$\Delta\Phi = \arctan\left(-\frac{Q}{2k} C' V^2\right). \quad (3)$$

where $C'$ denotes the second derivative of $C$ with respect to $z$. For a simple parallel-plate capacitor model, $C = \varepsilon_0 \frac{S}{d}$, where $S$ is the effective area of the parallel plate or, here, the area of the tip, $d$ is the effective distance between plates, or the distance between the tip and the sample, and $\varepsilon_0$ is the permittivity of air, we get

$$\Delta\Phi \approx -\arctan\left(\frac{Q \varepsilon_0 S E^2}{k d}\right), \quad (4)$$

where the electric field intensity $E = \frac{V}{d}$. For small angles, the phase shift is linearly proportional to the force gradient. As the probe is lowered down or the voltage difference between the probe and the sample increases, the electric field between the probe and the sample increases, and according to the above formulas, the phase shift increases. This relationship is useful only for qualitative phase-contrast measurements. The following paragraphs derive the absolute electrostatic force from the force gradient.

For the case that the grounded probe is scanned over the grounded wire, since the voltage difference between the probe and the sample is zero, the electrostatic force is
zero. The probe vibrates freely in air. Thus, the phase delay for the grounded probe over the grounded wire is \(-\pi/2\). The phase shift for the grounded wires should remain zero for different lift heights, which is contrary to our experimental results. As discussed above, it was observed that an offset existed in the phase shift of the grounded wire. Using differential mode between the phase shift at the charged wire and the phase shift at the grounded wire solved the problem of phase offset for the ground wires. We define the term phase difference to refer to the difference between the phase shifts between any two points.

We averaged the heights of the charged wire and the corresponding phase shifts in Fig. 1 (c). Taking into account the apparent height difference between the charged wire and the grounded wire, we plot the phase difference between the grounded wire and the charged wire vs. actual tip height curve, as shown in Fig. 2. The tip height includes the lift height for the dual-pass scheme operation and the apparent height difference. We have found that the height difference depends on the spring constant of the cantilever. For high values of the spring constant, for example about 4 N/m such as that for highly-doped silicon probes (TESP) from Veeco. Inc., the error in height is much smaller at the same applied voltage.

In the following paragraphs we obtain the force gradient from the phase difference. Equation (2) implies that

\[
\frac{dF}{dz} \approx -\frac{k}{Q} \tan(\Delta\Phi).
\]  

According the above formula, we can obtain the force gradient from the phase signal, as shown in Fig. 2. We have found that it is difficult to obtain the phase signal for lift heights below 50 nm because the electrostatic force is so strong that sometimes the
probe crashes into the surface. Also, above 300 nm it is difficult to distinguish the phase signal from the noise.

For any point above the charged wire, the z component of the electrostatic force is

\[ F = \int_{z}^{\infty} \frac{dF}{dz} \, dz. \]  \hspace{1cm} (6)

When the EFM probe is greater than 50 nm above the wire surface, which is much greater than its 10 nm radius, the probe can be modeled as a cone.

Fig. 6.2. Phase delay curve and force gradient curve at different height. The diamond-covered curve is phase delay signal; the circle-covered curve is force gradient curve.
We choose a cone model [19, 30],

\[
F_{cone}' = a + \frac{b}{z + c}.
\]  

(7)

where \(F_{cone}'\) is the force gradient sensed by the cone. Figure 6.3 shows that the force gradient derived from the cone-model curve fits the experimental data extremely well when \(a = -0.0009021\) nN/m, \(b = 1.082\) nN, and \(c = -6.473\) nm.

According to Eq. (7), the force gradient decreases to zero at a height of 1.206 μm and is not zero when the height is at infinity. Although the curve fits well within the experimental data range, we cannot determine the electrostatic force for all heights.

Fig. 6.3 Data fitting for force gradient data. The experimental data is in circles. The solid curve represents the fitting function.
Still, within the experimental range, the electrostatic force as a function of height can be accurately determined from,

$$F = \int_{z}^{308_{nm}} (a + \frac{b}{z + c})dz + F_{308_{nm}}. \quad (8)$$

where $F_{308_{nm}} = \int_{308_{nm}}^{\infty} \frac{dF}{dz}dz$. By integration of the force gradient $F_{\text{cone}}$ in Eq. (7) and choosing the upper limit of the integration as 1.206 $\mu$m, we obtain the force at a height of 308 nm (our highest measured value) as 0.682 nN. Above about 300 nm, it is difficult to determine the absolute electrostatic force because the signal-to-noise ratio degrades the measurement of phase shift.

Now we use finite element analysis (FEMLAB [31]) to obtain the electrostatic force at a height of 308 nm. Figure 4(a) shows the cone model used in the analysis. The mesh size at the apex of the probe in the model is 3 nm. The force in the vertical direction can be integrated over the surface of the probe [18, 20-21],

$$F = \int_{S} \frac{1}{2} E_z^2 \varepsilon_0 ds. \quad (9)$$

Using the parameters of 225 $\mu$m length, 30 $\mu$m width, and 10 $\mu$m height above the sample surface, we obtain the force on the cantilever about 0.007 nN by FEMLAB simulation. For the cone model, the height of the cone is 10 $\mu$m and the half angle is 20 degrees. The three wires are 3 $\mu$m long and 1 $\mu$m wide, and the middle wire is charged to 5 volts while the other two are grounded. The integrated force on the cone is about 0.085 nN. The sum of forces on the cone is $F_{308_{nm}} = 0.092$ nN. Now, according to Eq. (8), we obtain the electrostatic force curve shown in Fig. 4(b).
When the distance between the probe and the sample is below 100 nm, it is difficult to do finite element analysis with FEMLAB. The results are sensitive to mesh sizes and do not converge. With the solid model of the actual EFM probe constructed from SEM pictures of the EFM probe from different views, and with the mesh size down to below 1 nm, it might be possible to produce accurate electrostatic forces at different heights, and a more accurate curve than that of Fig. 6.4(b) could be obtained. The spring constant of the cantilever could be adjusted to fit this improved curve. The spring constant can be different from the value provided by the manufacturers or the theoretical calculation [32] due to the variable stoichiometry of the cantilever, humidity or air pressure, and the metal coating of the cantilever [33-35]. One might use the FEMLAB simulation data to calibrate the spring constant of the cantilever, which is of fundamental importance to the quantitative measurements.

Compared with KPFM as discussed in Chapter 3, the major advantages of EFM phase measurements are better lateral resolution due to force gradient detection and faster speed due to phase detection. Combined with Coulomb’s law, the measured electrostatic force can be used to count electrons on clusters as discussed in Chapter 3 for single electron detection. It is inconvenient that our EFM measurements automatically implement dual-pass scheme. Flexibility should be introduced to turn off the outside voltage sources during the first pass of the dual-pass scheme. Thus we can avoid the measurement error discussed in Chapter 5. Also, shell commands should be provided to perform complex measurements, for example, phase measurements at different lift heights.

The electrostatic force as shown in Fig. 6.4 (b) can be used to count electrons on nanoclusters, for example Co nanoclusters embedded in SiO2 deposited on an $n$-type Si substrate [36]. The charge $Q$ on Co nanoclusters induces image charge in the Si
substrate and the tip. Supposing this Co nanocluster layer \( d_1 \) distance from the surface and \( d_2 \) distance above the Si substrate, the tip \( h \) distance above the surface, according to an electrostatic analysis of a simple parallel-plate capacitor model, the force that the probe feels can be deduced as the following [36],

\[
F(h) = \frac{1}{\left( \frac{h + (d_1 + d_2)/\varepsilon_{\text{SiO}_2}}{\varepsilon_{\text{SiO}_2}} \right)^2} \times \left( -\frac{d_2^2}{\varepsilon_{\text{SiO}_2}^2 \varepsilon_0 A} + \frac{2d_2 Q V}{\varepsilon_{\text{SiO}_2} \varepsilon_0} + \frac{\varepsilon_0 A V^2}{2} \right),
\]  \hspace{1cm} (10)

where \( \varepsilon_{\text{SiO}_2} \) is the relative permittivity of SiO2 and \( A \) is the area of charged region. Thus \( Q \) can be calculated from Eq. (10) and the number of electrons on the nanoclusters is achieved.
Fig. 6.4. (a) Finite element analysis of electrostatic force; (b) Electrostatic force at different heights.
6.4 Quantitative electric field for QCA clocking circuits

As shown in Chapter 4.4.1, the tip of an EFM probe can be modeled as a point in the metal ground plane above the clocking wires, which is used to direct the electric field upward. In other words, from the viewpoint of the metrology, although the introduction of the EFM probe changes the electric field distribution, the electric field distribution is unique for every different height of the probe-sample distance. We can assume that the metal ground plane exists and the EFM probe is oscillating inside. For every different height of the probe-sample distance, we get a corresponding unique phase shifts. Thus, we can say that we can measure the electric field between the metal ground plane and the wire plane by the phase shifts.

In Fig. 6.5 (a), the electric field is for the tip of the EFM probe or a point on a metal ground plane, which is inversely proportional to the probe-sample distance. We obtained the electric field by simulation. As shown in Fig. 6.3, the force gradient or the phase shift is also nearly inversely proportional to the probe-sample distance. We get Fig. 6.5 (b) where the electric field is almost linearly proportional to the absolute value of the phase shift.

In summary, through our experimental and theoretical investigation, electrostatic force was quantified by EFM-phase measurements. We considered the variations in measured topography due to residual electrostatic force during the first pass of the dual-pass mode. Phase information was converted into the force gradient, which was then used to determine the electrostatic force between the probe and the sample as a function of lift height. Simulations based on a cone model of the tip were used to determine the constant of integration in the measurements. These experiments are the first to demonstrate quantitative force measurements based on phase information in EFM.
Fig 6.5. (a) The intensity of electric field between the metal ground plane and the wire plane obtained by simulation decreases with the increasing of the space between the two planes. (b) The electric field at the tip of the EFM probe, i.e. a point in the metal ground plane, increases with increasing of phase shift.
CHAPTER 7
CONCLUSIONS AND FUTURE WORK

For the purpose of clocking molecular QCAs, we have made progress in nanowire fabrication, EFM measurements, and computer simulations of the distribution of electric fields and the power consumption of clocked circuits. Conductive nanowires were fabricated in parallel by EBL and metal lift-off to make multiple-phase clocking circuits. Different voltages were applied to the nanowires to simulate different phases. EFM was used to detect the electric field from these voltage-applied nanowires. Many qualitatively phase-contrast images of clocking circuits have been obtained. For the first time, we have successfully demonstrated quantitative electrostatic force measurements based on phase information in EFM. Also a source of EFM measurement error has been pointed out.

For the following work, we must be concerned the conductance of narrow wires, the planarization for multilevel clocking circuits, and the possibility of Kelvin probe force microscopy detection of molecular switching. In order to make the whole circuit work, each nanowire in the circuit should be conductive. With the shrinking of the size of nanowires, large grain size and large inter-grain distance result in broken nanowires. We must address this problem and make a trade-off. Also we can possibly add a planarization layer above the clocking circuit. The electric field components on the plane of molecules cannot be ignored since these components can cause logic
miscalculations. Last, Kelvin probe force microscopy can be used to detect molecular switching.

7.1 Conductive nanowires for clocking circuits

The nanowires for clocking circuits must be not only as small as possible, but also, most importantly, conductive. As shown in Fig. 1.4, the nanowires consist of many metal grains. These grains are formed on the substrate after physical vapor deposition. These nanowires are discontinuous and cannot be conductive, although the widths of some nanowires are below 10 nm.

During the deposition process, the metal layer with large grain size will shrink open windows of PMMA trenches very quickly. Not only is the developer solution difficult to get inside the trenches, but also the developed PMMA is difficult to get out of the trenches. Large inter-grain distance causes many breaks along the nanowire, which results in an open circuit.

Thus, we need small grain size and also small inter-grain distance. The grain size depends on the temperature of the substrate, the deposition speed, and the film thickness. As shown in Fig. 7.1, the grain size decreases as the temperature of the substrate decreases, the deposition speed decreases and the film thickness decreases [1].

In Fig. 7.1 (a), for the deposition speed at 0.5 nm/s and the film thickness at 16 nm, the inter-grain distance is zero. The nanowire should be conductive if we deposit at least 16 nm thick gold at the speed of 0.5 nm/s. The wire aspect ratio is usually less than 1. In order to conduct electric current, the width of nanowires is around 16 nm. 16 nm nanowires can be fabricated by using the “mix and match” method, as discussed in Chapter 4. We also can use metals with smaller grain size, such as AuPd.
Fig. 7.1. Grain size dependence on the deposition speed, the film thickness and the substrate temperature (adopted from [1]). The metal for the film is gold on the glass substrate. \( r \) is the grain radius and \( d \) is the inter-grain distance. The deposition speeds are 0.5 nm/s and 0.05 nm/s. (a) Grain size decreasing with the decreasing of the deposition speed or the film thickness. (b) Gain size decreasing with the decreasing of the substrate temperature. Two films are 4 nm and 6 nm. The deposition speed is 0.05 nm/s.
7.2 Planarization for clocking circuits

We cannot deposit molecules directly on clocked nanowires. We need a flat and smooth plane to put molecules on. The dielectric layer between the plane and the clocking circuits can be $SiO_2$ or even PMMA. If $SiO_2$ is deposited, either by electron beam evaporation or chemical vapor deposition (CVD), we need chemical mechanical polishing (CMP) to polish the surface. Since the stress caused by CMP might damage our delicate nanowires, PMMA is recommended. Here, PMMA acts as a kind of spin-on-glass (SOG). The glass transition temperature (Tg) for PMMA is approximately $95-106^\circ C$ [2]. We bake PMMA above Tg, usually at $180^\circ C$ for 5 minutes, to drive off solvents and get a final flat and smooth surface.

With this flat and smooth surface, we can extend the previous EFM experiments discussed in Chapter 4. First, we can test the electrical navigation map for Fig. 4.7, instead of the geometrical map in Fig. 4.8. Parts of the PMMA layer will be exposed for bonding areas. Since the size of the area required by our bonding machine is greater than $100 \times 100 \mu m^2$, such a big area will take a long time for electron-beam exposure. Second, we want to verify the explanation for the results in Fig. 4.13 (b). With an additional PMMA layer now, if peaks or valleys of the electric field intensity disappear between the nanowires, it means that the EFM probe did sense strong electric fields there. Last, we can investigate the resolution of our EFM. A flat PMMA surface can prevent the introduction of geometrical effects into EFM imaging. The best resolution recorded so far is about 30 nm [3]. If 16 nm of conductive nanowires are fabricated and a flat PMMA is added, we can hopefully use our EFM to detect those electric fields emitted from the nanowires.
7.3 Electric field components on the plane of molecules

Since the length of clocked nanowires is not infinite, the electric field components running parallel to the nanowires cannot be ignored, especially at the ends of the clocked nanowires. The electric fields above the clocked nanowires have components in the plane of molecules. There are $E_x$ and $E_y$ components, as shown in Fig. 7.2. $E_x$ is parallel to the direction of molecules arrays. $E_y$ runs parallel to the nanowires. These components result in unequal potentials of dots in a molecular QCA, which could cause incorrect logic switching.

For cell $A$ and $B$ in Fig. 7.2, under the influence of $E_y$, the favorable positions for electrons are $A_{1c}$, $A_{2c}$, $B_{1c}$, and $B_{2c}$. Thus if the force from neighboring cells is not strong enough, the electron in $A_2$ will stay at the $A_{2c}$ dot. At the ends of the nanowires, $E_y$ shows more effect. When we calculate the proper working region, we have to take this effect into consideration.

The simulation program written in Matlab code is based on the charge simulation method. A four-phase clock signal [4-5] is used in the simulation. The Matlab code for the clock signal is adapted from QCACWEST [6]. The speed of simulations is greatly improved when we apply the method of matrix vectorization in the program.
Fig. 7.2: Molecular QCA cells above a clocked nanowire. There are two QCA cells, A and B. Each includes two half cells. Each half cell has three dots, a, b, and c. A1 half cell has A1a, A1b and A1c dots, etc.

7.4 Kelvin probe force microscopy detection of molecular switching

Kelvin probe force microscopy (KPFM) not only can measure contact potential differences between different metals, but also can measure the surface potential of self-assembled molecules [7-9]. The surface potential due to dipole properties of molecules is related to the inherent molecular structures, the orientation of the molecules, and the density of the molecules. As shown in Fig. 7.3 (a), for this dipole, point P is $r_+$ distance from the positive end and $r_-$ distance from the negative end. According to Coulomb’s law, the potential at the point of P,

$$\Phi_P = \Phi_+ + \Phi_-$$

$$= \frac{q}{4\pi\varepsilon_0} \left( \frac{1}{r_+} - \frac{1}{r_-} \right)$$

$$= \frac{q}{4\pi\varepsilon_0} \left( \frac{1}{r - \frac{d}{2}\cos\alpha} - \frac{1}{r + \frac{d}{2}\sin\alpha} \right)$$

$$\approx \frac{q\cos\alpha}{4\pi\varepsilon_0 r^2}$$
where \( q \) is the charge of the dipole, \( a \) is the angle of point P deviated from the vertical direction, which is zero when the point P is directly above the dipole as shown in Fig. 7.3 (b). For the current QCA molecule candidate, Fe-Ru complex [10], \( d=0.6 \text{ nm} \) and the complex is perpendicularly aligned to the surface. The KPFM probe is put directly over the dipole as shown in Fig. 7.3(b), where \( \alpha = 0 \). We get \( \Phi_p = 8mV \) if the tip is 10 nm high and \( \Phi_p = 2mV \) if the tip is 20 nm high.

For the sensitivity of KPFM, the theoretical limit of the minimum detectable surface potential [11],

\[
V_{\text{min}} = \sqrt{2k_BTkB / \pi^3Qf_{\text{res}}(1 / \varepsilon_0V_{\text{AC}})(d / R)}.
\]  

(2)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( k \) is the spring constant of cantilever, \( B \) is the instrument bandwidth, \( Q \) is the cantilever quality factor, \( f_{\text{res}} \) is the resonant frequency of cantilever, \( d \) is the tip-to-sample distance, \( V_{\text{AC}} \) is the oscillating voltage applied to the probe, and \( R \) is the tip radius. For our highly-doped silicon probes, \( k=44 \text{ N/m}, Q=455, d=20 \text{ nm}, R=10 \text{ nm}, f_{\text{res}}=300 \text{ kHz}, V_{\text{AC}}=2 \text{ volts}, \) and \( B=1 \text{ Hz}, \) we get \( V_{\text{min}}=1.35 \text{ mV} \). Thus we can detect a single Fe-Ru complex with our KPFM. However, the exact location of the probe over the complex is difficult. To detect a cluster of such complex as shown in Fig. 7.3 (c) is a possible easier way.
Fig. 7.3 Schematic picture of a dipole molecule (a), with the introduction of the probe of KPFM (b), and a cluster of dipole molecules (c).
Supposing the vector of dipole \( \vec{d} \), the density of dipole vector is
\[
\rho_s = \frac{\sum q \vec{d}}{\pi R^2}.
\] (3)

where \( R \) is the diameter of the cluster. The potential at \( H \) height above the sample plane that the probe senses can be computed with following integration equation,
\[
\Phi = \int_0^{2\pi} \int_0^R \frac{\rho_s \cos \beta}{4\pi \varepsilon_0 l} dr d\theta
\]
\[
= \int_0^{2\pi} \int_0^R \frac{\rho_s H}{\sqrt{r^2 + H^2}} dr d\theta
\]
\[
= \frac{\rho_s}{\varepsilon_0} \left\{ \frac{1}{1 - \frac{1}{\sqrt{\left(\frac{R}{H}\right)^2 + 1}}} \right\}
\]
\[
\approx \frac{\rho_s}{\varepsilon_0}
\] (4)

With the density of Fe-Ru complex at \( 4 \times 10^{17} / m^2 \), we get
\[
\Phi = \frac{4 \times 10^{17} \times S \times 1.60 \times 10^{-19} \times 0.6 \times 10^{-9}}{S \times 8.85 \times 10^{-12}} = 4.339 \text{ volts}, \text{ where } S \text{ is the area of the cluster.}
\]
The result is nearly the same as that from equations calculated by commercial Gaussian 98 software [7, 8] except the permittivity of the complex \( \varepsilon_{Fe-Ru} \).

Considering \( \varepsilon_{Fe-Ru} = 2.6 \), we get \( \Phi = \frac{4.339}{2.6} = 1.63 \text{ volt, which can be easily detected by KPFM.} \)

QCA molecules can be selectively grown on clocking wires fabricated by electron beam lithography and metal lift-off. Applying voltages to these wires switches the dipole properties of the molecules. Different intensity of electric field results in different directions of dipole vector. Thus it forms voltage contrast, which can be detected by KPFM. By this method, we can measure the critical intensity of electric field that can switch the molecule; also we can test the duration of unstable states where the molecules take a stop to stable states.
A simple experiment is proposed here to demonstrate the detection of molecular switching by KPFM or EFM. Fig. 7.4 (a) shows the potential distribution of 55 nm wide three metal nanowires and 145 nm thick silicon dioxide substrate. The middle nanowire is applied with 30 volts while the other two are grounded. The space between the nanowires is 55 nm. The height of the nanowires is 55 nm. The $E_z$ distribution at 1 nm above the plane of the nanowires is shown in Fig. 7.4 (b). The top two points of the $E_z$ curve correspond to the two edges of the middle nanowire.

Assuming the critical switching point $E_0$ at 4 Mv/m for our particular molecules, the molecules get switched if they sense $E_z$ that is greater than $E_0$. The switched and non-switched molecules across the surface of the middle nanowire produce different surface potentials that can be picked up by KPFM. This potential difference can also be detected by EFM-phase measurement. We can measure the switching point of molecules by increasing the voltage of the middle nanowire until the voltage difference or phase contrast occurs.

In summary, we investigated nanowire fabrication, EFM measurements, and computer simulations of the distribution of electric fields. Quantitative EFM-phase measurements have been demonstrated. For future work, we discussed the conductance of QCA clocking nanowires and the non-vertical electric field components. Also, the possibility of detecting molecular switching by KPFM was investigated.
Fig. 7.4. The potential distribution of 55 nm wide nanowires (a) and $E_z$ distribution at 1 nm above the plane of the nanowires (b), where the vertical axis unit is v/m and the horizontal axis is the number of position points.
Fig. 7.5. $E_z$ distribution above the middle nanowire as shown in Fig. 7.4 (a) at the top and surface potential detected by KPFM across the middle nanowire at the bottom.
APPENDIX A
POWER CONSUMPTION OF CLOCKED NANOWIRES

The power consumption mostly comes from the charging and discharging of clocked nanowires. We start the calculation of power consumption with 50 nm nanowires because they can be easily made in our lab by the Amray EBL. According to the International Roadmap for Semiconductors [1], this scale can be reached by 2010.

As shown in Fig. A. 1, a non-zero voltage is applied to a nanowire and the sample is grounded. The electric field concentrates in the region directly below the nanowire. Electric field outside the region is called fringing electric field. According to the formula [2], the equation of the wire is

\[
C_{\text{wire}} = C_{\text{parallel}} + C_{\text{fringe}} = \varepsilon \left[ \frac{w - t / 2}{h} + \frac{2\pi}{\ln \left( 1 + \frac{2h}{t} + \sqrt{\frac{2h}{t} \left( \frac{2h}{t} + 2 \right)} \right)} \right]. \tag{1}
\]

\(C_{\text{parallel}}\) is the capacitance for the region directly below the nanowire and \(C_{\text{fringe}}\) is the capacitance outside that region. \(\varepsilon\) and \(t\) are the permittivity and the thickness of the dielectric \(SiO_2\) and \(w\) and \(h\) are the width and height of the nanowire. Eq. (1) is for a single wire. For many nanowires in parallel, we have to consider the coupling capacitance between nanowires [3]. The capacitance between nanowires is

\[
C_{\text{interwire}} = \frac{\varepsilon h}{d}. \tag{2}
\]
Thus the total capacitance is

\[ C_{\text{total}} = C_{\text{parallel}} + C_{\text{interwire}} + C_{\text{fringe}}. \]  

(3)

With \( w = 50 \) nm, \( t = 50 \) nm and \( h = 110 \) nm, Eq. (1)-(3) yield

\[ C_{\text{total}} = 144 \ \mu F/\mu m. \]  

(4)

For the resistance,

\[ R_{\text{wire}} = \frac{\rho_{\text{wire}}}{s} \cdot \frac{l}{s}. \]  

(5)

where \( \rho_{\text{wire}} \) is the resistivity coefficient of the nanowire; \( l \) and \( s \) are the length and cross-sectional area of the nanowire. Due to surface scattering, the resistivity of nanowires is larger than the bulk resistivity for gold [4].

Supposing \( \rho_{\text{wire}} = 3 \rho_{\text{bulk gold}} = 6.6 \ \mu \Omega \cdot cm \) [4] into eq. (5), we get

\[ R_{\text{wire}} = 2.6 \times 10^7 \ \Omega / m = 26 \ \Omega / \mu m. \]  

(6)

1 cm x 1 cm chip with a 100 nm pitch and 1 \( \mu m \) long nanowire [5] would need about \( 8 \times 10^8 \) wires/chip. The adiabatic power dissipation is
\[ P_{\text{dissip}} = \left( \frac{RC}{T} \right) \left( CV^2 \right) f, \]  \tag{7}

where \( T \) is the time for one cycle and \( f \) is the working frequency and \( C \) is the total capacitance for all nanowires on this chip. Taking Eq. (4) and Eq. (6) into Eq. (7), with a working frequency at 10 \( G \) Hz and a voltage of 1 \( V \), we get

\[
P_{\text{total}} = 8 \times 10^8 \frac{\text{wires/\text{cm}}^2}{\text{chip}} \times \left( R_{\text{wire}} C_{\text{total}} f^2 \right) \left( C_{\text{total}} V^2 \right).
\]

\[
= 4.5 \times 10^{-2} W. \tag{8}
\]

We applied the above formulas for different sizes of nanowires and different frequencies. As shown in Tab. A.1, we obtain the power dissipations for 10 nm, 20 nm, 50 nm and 100 nm nanowires at 1 \( G \) Hz, 10 \( G \) Hz, 100 \( G \) Hz and 1000 \( G \) Hz. Each nanowire is 1 \( \mu \text{m} \) long. The space between rows of nanowires is 0.25 \( \mu \text{m} \).

**TABLE A.1**

**POWER DISSIPATION OF CLOCKED CIRCUITS**

<table>
<thead>
<tr>
<th></th>
<th>10 nm</th>
<th>20 nm</th>
<th>50 nm</th>
<th>100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 GHz</td>
<td>5.7×10⁴ W/cm²</td>
<td>6.9×10⁴ W/cm²</td>
<td>4.5×10² W/cm²</td>
<td>57 W/cm²</td>
</tr>
<tr>
<td>100 GHz</td>
<td>5.7×10² W/cm²</td>
<td>69 W/cm²</td>
<td>4.5 W/cm²</td>
<td>0.57 W/cm²</td>
</tr>
<tr>
<td>10 GHz</td>
<td>5.7 W/cm²</td>
<td>0.69 W/cm²</td>
<td>4.5×10⁻² W/cm²</td>
<td>5.7×10⁻² W/cm²</td>
</tr>
<tr>
<td>1 GHz</td>
<td>5.7×10⁻² W/cm²</td>
<td>6.9×10⁻³ W/cm²</td>
<td>4.5×10⁻⁴ W/cm²</td>
<td>5.7×10⁻⁵ W/cm²</td>
</tr>
</tbody>
</table>

Tab. A.1: Power dissipations in watts per square centimeters (\( W/cm² \)) for 10 nm, 20 nm, 50 nm and 100 nm nanowires at 1 GHz, 10 GHz, 100 GHz and 1000 GHz.
APPENDIX B
ELECTRIC FIELD FOR PROGRAMMABLE LOGIC ARRAY IN QCA

For a QCA majority gate, when one input is at logic “1”, other two inputs can function as an OR gate; when one input is at logic “0”, other two inputs can function as an AND gate. Programmable logic array consists of an AND plane and an OR plane. QCA cells can be used to construct a PLA array, which was proposed by X. S. Hu, et. al [1]. The signal transports from the AND plane to the OR plane. The OR line selects AND lines. As shown in Fig. B.1 (a), the top majority gate acts as an AND gate because of one input at logic “0”; the bottom majority gate acts as an OR gate because of one input at logic “1”. The squares with four dots are QCA cells.

If the select bit is at logic “1”, the bottom majority gates now have two inputs at logic “1”. So the output of the bottom majority gate will be logic “1”, no matter what logic state that the LiteralIn is. Thus MintermIn = MintermOut if the select bit is at logic “1”. The PLA cell works as a wire connecting from MintermIn to MintermOut. If the select bit is at logic “0”, MintermOut will be at logic “1” only when MintermIn and LiteralIn are all at logic “1”. So MintermOut = MintermIn • LiteralIn. The PLA cell works as an AND gate. The logic representation of the PLA cell made of QCA cells is shown in Fig. B.1 (b).
Fig. B.1. (a) PLA cell in the AND plane. (b) Logic representation of (a). (adopted from [1]).

Programmable means rewritable. The select bits can be the outputs of OR gates as shown in Fig. B.1 (a). The programmability exploits the bi-direction properties of QCA wires. The reverse clocking electric field will be applied with proper settings for these OR gates. Switching the top majority gate and the bottom majority results in an OR gate. Complex logic functions can be implemented by PLA array constructed by AND gates and OR gates. As shown in Fig. B.2, an XOR logic function is demonstrated.
Fig. B.2. XOR function implementation of PLA array (adopted from [1]).

For normal operation this XOR function in Fig. B.2, the signals or the inputs transport rightwards; the sum of these signals moves downwards.

Supposing $T_{L1} = T_{L2} = T_{L3} = 1, T_{T5} = T_{T6} = 0, T_{B1} = X, T_{B2} = X', T_{B3} = Y, T_{B4} = Y'$, we get

$T_{B5} = T_{B2} \cdot T_{B3} + T_{B1} \cdot T_{B4}$, i.e. $T_{B5} = X'Y + XY'$. Thus an XOR logic function is implemented. Other complex combinations can also be realized this way.

How do we hold these select bits during the pipeline operation with the multiple-phase clocking electric field? A specially designed clocking signal is used as shown in Fig. B.3. In order to hold the logic state of QCA cells for select bits, we adopt two kinds of control signals. We use the electric field emitted from a clock circuit to control the flow of pipeline operation of QCA cells. Fig. B.3 shows the final level of such a circuit with two sizes of metal bars.
Fig. B.3. Geometry of the top level of clocking circuit. The shaded shape is the ground plane. The small cubes are applied with strong electric field to hold the select bits. The long wires are applied with multiple-phase clocking electric field. The unit is $\mu m$.

The circuit occupies460 nm by 460 nm area. The unit is $\mu m$. Short bars are 80 nm apart in horizontal direction and 80 nm apart in the vertical direction. All are to scale in Fig. B.3. According to ITRS 2004 for 2018 technology node, we choose 20 nm for the width and length of short bars and 20 nm for the width of long bars. The thickness of those bars is 10 nm. A metal plane is added 20 nm above those bars to act as the ground plane to direct the electric field. QCA cells are placed in the mid of the bars and the ground plane, i.e. 10 nm above the bars. Two kinds of clocking signals are applied: a constant voltage on short bars and a quasiadiabatic [2] signal on long bars.

FEMLAB software [3] is used to obtain the electric field distribution at the plane where QCA cells reside. Since a vertical component of the electric field is chosen to manipulate QCA cells, we are concerned only with the distribution of the vertical electric field. Supposing the intensity of 2 M $v/cm$ is enough to lock QCA cells, 5 volts
is used for the constant signal. We choose five different values of the quasiadiabatic signal applied on the long bars at -5 volts, -2.5 volts, 0 volt, 2.5 volts, and 5 volts. We use silicon dioxide as the dielectric with the relative permittivity at 3.9 and choose gold as the metal for the bars.

The simulation result in Fig. B.4 with five pictures shows two different partitions with two different clocking patterns. The geometrical contour of the bars is also shown in the pictures. We can see that the vertical electric field above the long bars changes from -2.5 M \text{v/cm} to 2.5 M \text{v/cm} while the vertical electric field above the short bars is unchanged. The intensity above short bars exceeds 2 M \text{v/cm}. The states of QCA cells are in “locked” states. During these states, QCA cells cannot receive any inputs and remain as their previous logic states. Thus the QCA cells above the short bars can be hold for select bits. The simulation demonstrates the ability to individually control the electric field to implement the select bits.
Fig.B.4. Vertical electric field distribution at the plane of QCA cells. The scale bar is from -3 M v/cm to 3 M v/cm. The geometrical contour of the bars is also shown in the pictures. The area is 460 nm by 460 nm. (a)-(e) correspond to five different times of a quasiadiabatic signal applied on the long bars at -5 volts, -2.5 volts, 0 volt, 2.5 volts, and 5 volts.
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Chapter 1


Chapter 2


Chapter 3


Chapter 4


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Chapter 5


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Chapter 7


Appendix A


[5] Discussions with Dr. Lent and Dr. Bernstein.

Appendix B

