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Label-Free THz-Optoelectronic Sensing of Ultra-Low  
Concentration of Genetic Sequences: Theoretical Treatment

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## Abstract

An engineering and mathematics research project is performed to develop the science base and simulation capability for the study, analysis and design of highly-integrated and molecular-based information processing systems. Specifically, this research investigate MQCA architectures as a potential new paradigm for information processing through the development of: (1) detailed models of the interacting molecular-level components, and (2) robust simulation algorithms that are capable of treating phenomenon associated with nonlinear dynamical complexity. Here, it is crucial to understand the interaction between the molecular devices and the substrates. To this connection, we analyze the electrostatic characteristics of the tether atoms connecting organic molecules onto silicon (100)  $\sqrt{2} \times \sqrt{2}$  surfaces, which is a key factor in the design of molecular devices for information processing and biomolecular sensing. Design principles for silicon surfaces with required electrostatic functionality are presented.

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## §1. Introduction and Scientific Background

Complexity of physical systems is becoming increasingly more important in the context of modern information processing system [1]. The demand for complexity research in nanometer-scale information processing system has originated from the scaling of devices which leads to extremely complicated circuit structures and versatile new functionality even in the context of traditional semiconductor electronics. Specifically, digital information processing systems based on CMOS transistors face new challenges as the limits of down-scaling come into view. With the scaling of the gate length of transistors down to 9nm, quantum tunneling effects and heat dissipation in the type of systems will greatly downgrade the functionality of information processing systems. Thus, CMOS scaling will likely become very difficult at and beyond the 9nm physical gate length limit (i.e., 22 nm node) [2~5]. In such situations, energy dissipation in nanoelectronic based systems is becoming a main concern in current research of low-energy-consumption information-processing systems. As will be shown, the demands associated with the design of these types of information processing systems have invoked a critical need for the understanding of the complexity in nanoscale and molecular-level devices and circuits.

Digital information processing systems benefit from scaling of devices in device switching time and integration density. To extend the benefits of scaling beyond the 9nm physical gate length limit, it is crucial to explore alternate physical mechanisms for device operation [2, 6]. Quantum dot cellular automata (QCA) based circuits are one of the device concepts proposed for solving the problem of information processing beyond the physical gate length limit [7]. In the QCA concept, circuits are composed of cells interacting by Coulomb interaction. However, the physical features and functionality of individual units are determined by the collective features of the entire system. Thus, a QCA circuit is a very complex system. From the point of view of electrical engineering research, it is important to understand the design criteria for the QCA circuits and the circuit physics. Here, the dynamical complexity of the circuits, indicated by Lyapunov exponents and a local generalization of the Kolmogorov entropy which are closely related to energy dissipation in the system [8, 9], play important roles in determining the criteria.

The basic device concept for QCA was first suggested by Lent et al. in 1993 [7]. Quantum cellular automata composed of nanometer-scale quantum devices (quantum dots) coupled through carefully chosen hopping and Coulomb interactions. It encodes classical binary information in different charge configurations of the system. The typical basic element in these QCA is a cell consisting of four dots located at the vertices of a square and connected via tunneling barriers to their neighbors. Electrons are able to tunnel between the dots, but do not leave the cell.

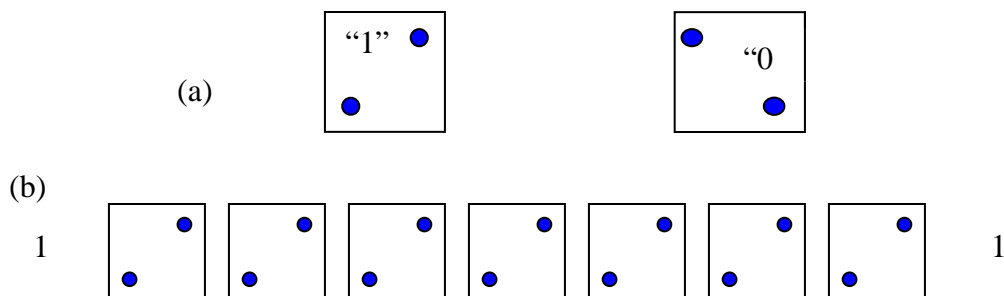


Fig. 1. (a) Polarizations and logic states of the cells of quantum dot cellular automata, and (b) binary wire of quantum dot cellular automata.

If two extra electrons are placed in a cell, Coulomb repulsion will force the electrons to the opposite spatial corners. There are thus two energetically equivalent ground state polarizations, as shown in Fig. 1(a), which can be labeled logic “0” and “1”. By placing such cells in a line and polarizing the first cell with an external electric field, one can propagate the polarization along the line (see Fig. 1(b)) *thereby transferring information without using “conduction” currents* [10]. By arranging line of cells one can build logical gates [11]. Experimentally, prototypes of metallic QCA cells and QCA circuit that possess 200 of these cells has been demonstrated [12]. Evidence for the transfer of polarization in QCA (and therefore information) has also been shown [13]. Thus, this computing paradigm provides a possible route to transistor-less electronics at nanometer scale [14] with reduction in energy generation via the elimination of conduction current.

While this computing paradigm exhibits the provocative features in switching time and device density, metallic QCA circuits has some fatal drawbacks. For examples, the metallic QCA circuits require cooling to less than 1mK to avoid random switching of the circuit [13]. Theoretically, if the size of the cell is small enough, say approximately 2 ~ 3 nm per side, the device could function at room temperature. However, it is extremely hard to make clusters of metal atoms of this small reproducibly enough not to introduce any inherent bias. On the other hand, the dimension of this QCA cell is on the typical size of molecules, which are much more amenable to make reproducibly, and opens the door for possible molecular implementation of the QCA concept if new insights into their operational characteristics can be developed.

In order to fabricate QCA circuits functioning at room temperature, the concept of molecular QCA (MQCA) was suggested by Lent and his co-workers [15, 16]. In a MQCA cell, the dots are redox centers in a molecule which can be occupied by, for example, one or two electrons (or holes). Some implementations have four redox centers in the molecule, resulting in one molecule per cell. In this previous analysis, the fundamental operational principle of the MQCA circuits was interpreted in terms of the interaction between electrons in the molecules and a *static electrical field*. It is important to note that the primary interaction between MQCA cells is actually due to *displacement currents* that arise out of time-dependent electromagnetic fields and this subject will be discussed later when emphasis areas of the proposed research are discussed. Specifically, the vertical component of the external field was viewed as controlling the occupation of the dots, which leads to the switching during periods when the dots are occupied. While the vertical component of the field controls the switching of the MQCA, the horizontal

components of the field which was contributed by the neighbor cells, determines the polarization of the cell thereby the representation of a logical 1 or 0 in the cell (see Figure 2) [17]. Mixed-valence transition metal complex molecules are believed to be suitable candidates for the quantum dots [18~21]. A conceptual architecture for molecular computing using MQCA's has also been recently suggested [22]. Furthermore, experimental research on electric field driven switching of a silicon surface bound array of vertically oriented two-dot MQCA has been conducted [23].

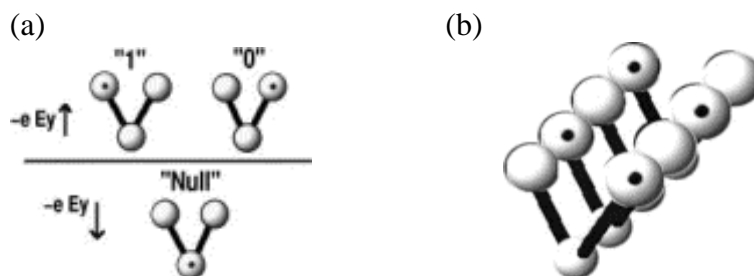


Figure 2. (a). Effects of vertical electric field on molecular charge configuration. (b). Illustration of suggested molecular wire with two cells.

The concept of MQCA circuit opens a door for possible solution of information processing beyond the physical gate length of 9nm limit. It is believed that this computing paradigm may lead to possible speed increase of 100 ~ 10000-fold over today's processors [24]. Thus, it is really a provocative computing concept that is drawing new attention. On the other hand, a MQCA circuit that contains very large numbers of molecules leads to an extremely complicated system and introduces new and challenging theoretical issues. Specifically, detailed insights into the dynamical behavior of such densely integrated systems will be a crucial element to the future design and analysis of MQCA information processing systems. In general, the problem presented is a complex dynamical system where the time-dependent nature of the global state of the system is determined by the interactions and coupling of local states. Here, the dynamics of the system, i.e. the change of the states of the system depending on time, is given by large coupled systems of nonlinear differential equations. Thus, while MQCA circuits are ideal prototypes for nanoscale computing and data processing architectures, they also present a unique example of large-scale nonlinear dynamical systems for computational mathematical research. In addition, as will be shown later, the MQCA research problem represents one of maximum dynamical complexity where nonlinearity, nonlocal interactions and memory play a dominate role.

## §2. Theoretical Model and Research Method

### A. Physical Model for MQCA

The system to be studied in this proposal is composed of molecules that exhibit quantum mechanical characteristics that are coupled via classical electromagnetic fields. Thus, the mathematical model for describing the system should involve the theoretical methods that can correctly describing the both the quantum-based molecules and the electromagnetic field, respectively.

Density Functional Theory (DFT), where the electronic density plays the central role, has been extensively used in recent years for the simulation of molecular and nano-scale systems with great success [25]. DFT advantages include: (1) a more intuitive 3-D density than the alternative N-particle 3-D wavefunction, (2) *computational simplicity*, and (3) the capability to handle infinite periodic systems and non-periodic systems of very many atoms ( $>10^3$ ). Thus, DFT is a suitable tool for describing a system with a large number of atoms. Hence, the molecule subsystem of MQCA can be described by DFT in this research.

In density functional theory, the time-dependent Kohn-Sham equation can be written as [26],

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\vec{r}, t) + v_E(\vec{r}, t) + \bar{v}_{xc}(\vec{r}, t, n) + v_{Hartree}(\vec{r}, t, n) \right) u_i(\vec{r}) = i\hbar \frac{\partial}{\partial t} u_i(\vec{r}) \quad (1)$$

where

$$v_{ext}(\vec{r}, t) = \sum_{\alpha} \left[ v_{local}^{\alpha}(\vec{r}, \bar{R}_{\alpha}) + v_{non-local}^{\alpha}(\vec{r}, \bar{R}_{\alpha}) \right] \quad (2)$$

In this formula,  $v_{local}^{\alpha}(\vec{r}, \bar{R}_{\alpha})$  is the local part of the pseudopotential of the nucleus  $\alpha$  at the position  $\bar{R}_{\alpha}$  and  $v_{non-local}^{\alpha}(\vec{r}, \bar{R}_{\alpha})$  denotes the non-local part of the pseudopotential which is used in the original Kleinman-Bylander form,

$$v_{non-local}^{\alpha}(\vec{r}, \bar{R}_{\alpha}) = \sum_{lm} \frac{|\phi_{lm}(\vec{r}) \delta V_l(\vec{r}) \rangle \langle \phi_{lm}(\vec{r}) \delta V_l(\vec{r})|}{\langle \phi_{lm}(\vec{r}) | \delta V_l(\vec{r}) | \phi_{lm}(\vec{r}) \rangle}, \quad (3)$$

where  $\phi_{lm}$  are the atomic pseudo-wave functions of angular momentum  $l$  and  $m$ , and  $\delta V_l$  is the difference between the pseudopotential that generates  $\phi_{lm}$  and  $v_{local}^{\alpha}(\vec{r}, \bar{R}_{\alpha})$ .  $v_{xc}(\vec{r}, t, n)$  is the time-dependent exchange-correlation (xc) potentials defined as

$$v_{xc}(\vec{r}) = \frac{\delta A_{xc}[n]}{\delta n} \quad (4)$$

Here,  $A_{xc}[n]$  is the exchange-correlation part of the quantum mechanical action of the electronic system.  $v_E(\vec{r}, t)$  is the interaction potential between electron and the electromagnetic field, which is given by

$$v_E(\vec{r}, t) = \vec{E}(t) \cdot \vec{r}. \quad (5)$$

Furthermore, the Hartree potential is obtained as the solution of the Poisson equation

$$\nabla^2 v_{Hartree}(\vec{r}, t) = -4\pi n(\vec{r}, t). \quad (6)$$

Here, time is treated as a parameter since the speed of electrons is greatly less than that of light. In terms of the K-S orbits, the current density and the charge density can be expressed, respectively, as

$$\vec{J} = \frac{1}{2i} \sum [u_k^*(\vec{r}, t) \nabla u_k(\vec{r}, t) - u_k(\vec{r}, t) \nabla u_k^*(\vec{r}, t)] \quad (7)$$

and

$$n(\vec{r}) = \sum_{i=1}^N |u_i(\vec{r})|^2 \quad (8)$$

In dealing with the motion of the nuclei, the quantum feature of the nuclei is neglected. Thus, the motions of the nucleus subsystem of MQCA can be described by Newton's equation.

$$M_J \frac{d}{dt} V_J = - \frac{\partial}{\partial R_J} E_0(\{R_J\}) \quad (9)$$

$$V_J = \frac{dR_J}{dt}$$

where  $R_J$ ,  $Z_J$ , and  $M_J$  are the coordinates, charge numbers, and masses of the  $N$  atoms, respectively, and  $E_0(\{R_J\})$  is the ground state energy of the system.

In a molecular system, the electromagnetic radiation is produced by the transition of electrons from higher energy state to a lower energy state. Here, for simplicity, the radiation will be described by classical electromagnetic theory. This simplification is reasonable as the motion of electrons will lead to the change of the distribution of charges and current density in MQCA circuits. Thus, electromagnetic field, coming from the radiation of the molecules while the high frequency logical signals are propagating in the system, can be described by the Maxwell equations.

$$\nabla \times \vec{E} = -\mu \frac{\partial \vec{H}}{\partial t} \quad (10)$$

$$\nabla \times \vec{H} = \vec{J} + \varepsilon \frac{\partial \vec{E}}{\partial t}$$

where  $\mu$  denotes the permeability and  $\varepsilon$  the permittivity. The current density is defined by Eq. (7). The above stated equations defined a self-consistent model for describing the MQCA circuits while high frequency clocked signals are propagating in the circuits. Here, Kohn-Sham equation and Newton's equation defined the dynamical systems for electrons and ions, respectively. The solutions of the equations will provide quantities for further evaluation of the properties of the MQCA circuits, such as the heat generation and dissipation, the quantum and the classical complexity, the intrinsic indicators of dynamical complexity (Lyapunov exponents and Kolmogorov entropy), chaos interaction and propagation of signals in the circuits. These results will be used to analyze the operational mechanism of the MQCA circuits based on dynamical theory, as well as the heat management methodology for the system.

## **B. Numerical Methods**

The success of this project depends on the numerical solution of the model stated above which we already know will be complicated by the effects of complexity. Specifically, MQCA circuits are extremely large and complicated systems that incorporate the effects of nonlinearity, nonequilibrium, nonlocality and memory. Also as stated previously, the simulations associated with this research will deal with very large numbers of interacting molecules that are subject to clocked excitations. Thus, an effective algorithm for solving the dynamical model is the key to the success of this project. In our previous research, we have successfully developed several algorithms for solving time-dependent problems in quantum device simulation [27,28]. Our algorithms have demonstrated increases of the computing speed a factor of 100 as compare to implicit algorithm in time integration on a single processor. To solve the nonlinear equations that arise in the time integration of our prior problem, the code VODEPK [29,30] was applied which uses a Newton-GMRES algorithm. The major focus of this work was preconditioner development and was based upon previous experience with large systems of linear equations [31].

## **§3. Achievements of the Proposed Research**

### **A. Design Methodology of Highly-Sensitive Surfaces of Substrates for Fabrication of M-QCA Devices and Circuits**

To be eligible for processing information in M-QCA computing paradigm, a M-QCA cell must meet the criteria below: 1) a stable mixed-valence state with a comproportionation constant of at least  $10^3$ ; 2) strong coupling between the sites; 3) capability of functionalization for surface binding in ordered arrays; 4) a good preparative route from readily accessible starting materials; 5) the capability for realization of clocking of M-QCA circuits; and 6) kinetic stability associated with degradation reactions [32, 33]. Currently, the searching for suitable molecules for M-QCA computing focuses on hetero-bimetallic and unsymmetrical complexes, homo-metallic complexes, and endohedral fullerenes [32 ~ 36].

In previous theoretical research for hunting suitable mixed-valence transition metal complex molecules for QCA cells, the molecules are treated as isolated clusters [35, 37]. In real practice, the molecules have to be immobilized or to be bonded to the surface of substrates. Thus, the linker molecule will influence the charge distribution in the complexes. Furthermore, the charges in the molecules may transfer from the molecules to the substrates. These effects can change the energy structure of the cells and lead to different selection of the mixed-valence transition metal complex molecules for QCA cells and circuits. On the other hand, clocked QCA circuits are elements for processing information in this computing paradigm. The clocked signals influence the charge distribution on the surface of substrates, thereby affecting the transfer of charge through the linker molecules and the polarization of the charges in the complexes. Thus, the study of the attachment of organic linker molecules to the surface of substrates is an important issue in realizing the M-QCA computing paradigm. This study is also of importance to other future nanotechnologies such as the highly integrated chemical and biological sensors and molecular electronic devices. Systematic study on the electrical properties of the self-assembled

organic monolayer on the surface of semiconductors should also extend our understanding of electron transfer through organic/inorganic heterojunctions [37].

Experimentally, mixed-valence transition metal complexes, such as hetero-bimetallic, unsymmetrical Ru-Fe complex,  $\text{trans-RuCl}(\text{dppm})_2 - (\text{C}\equiv\text{CF}_c)$ , where  $F_c = (\eta^5 - \text{C}_5\text{H}_5)$   $F_c(\eta^5 - \text{C}_5\text{H}_5)$ ,  $\text{dppm} = \text{methyl/bis (diphenylphosphane)}$ ;  $[(\text{acac})_2\text{Ru}(\text{bptz})\text{Ru}(\text{acac})_2]^{0,1+}$ ,  $\text{acac} \equiv \text{acetylacetonate}$ ,  $\text{bptz} \equiv 3, 6, \text{-bis(2-pyridyl) - 1, 2, 4, 5 - tetrazine}$  are immobilized onto the surfaces of gold and silicon (111), respectively, via linker molecules, such as alkyl chains [38]. As indicated by Ref.33, clocking wires are needed to be embedded in the substrate to provide signals to control the status of the QCA cells, thereby effectively governing the propagation of signals in QCA circuits. As shown by above stated experiments, alkyl chains have been used to immobilize the MVTMC. Physically, the effects of the clocking field on the status of the QCA cells are dependent on the length of the chains. Thus, the length of alkyl chains is a factor affecting the operation of QCA circuits. Furthermore, since alkyl chains are insulators, the clocking field cannot effectively influence the status of the QCA cells. To effectively control the status of the QCA cells, thereby the propagation of signal in the circuits,  $\pi$ -conjugated systems should be used as the linker molecules to immobilize the MVTMC.

The attachment of  $\pi$ -conjugated molecular systems on the surface of substrate has become a research interests in recent a few years [39 ~ 41]. Theoretical and experimental researches show that  $\pi$ -conjugated molecular systems can be absorbed onto the surface of silicon (100) surfaces via direct Si – C linkage [42], Si – S linkage [43], Si – N linkage [44]. Previous research of the attachment of  $\pi$ -conjugated system to the surface of silicon mainly focus on the binding geometrical structures and the stability of the structures. In this paper, we discuss the electrical behaviors of the systems. Specifically, we are interested in the answers of the following questions: 1). which is the most electrically effective binding structures? 2). how to realize the Ohm contact or the Schottky contact in aromatic molecule – silicon systems. The answers to these two questions are important not only to the integral architectures for QCA based molecular computing, but also to the research of transport through molecular devices because a correct boundary condition to the model of molecular devices, or the electrical characteristics of the interface between the surface of the substrate and the self-assembled molecular monolayer is crucial to reproduce experimental results.

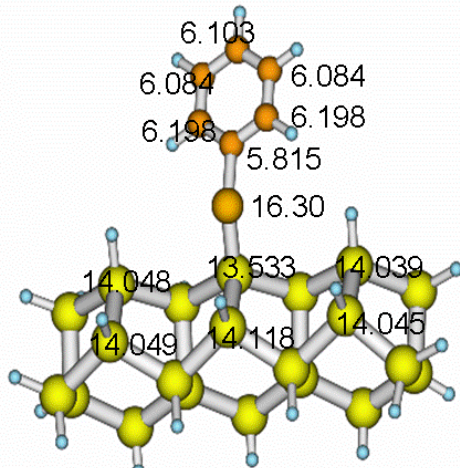
In this study, in terms of time-independent density functional theory, we will study the attachment of  $\pi$ -conjugated system on silicon (100) –  $2 \times 1$  surface. Since the fabrication of a  $\pi$ -conjugated molecule system on silicon surface is the first step in realizing molecular computing, we discuss the electrical characteristics of the attachment of aromatic molecules on silicon surfaces. Here, we have picked silicon as the substrate because Silicon (100) surfaces play a decisive role in many technologically important device applications. The structure of the surface has been widely studied, both experimentally and theoretically [45 ~ 47]. The knowledge of the surface provides a good reference for the study of the interactions of the surface and the complex molecules. Thus, in this research, we investigate the issue of attachment of aromatic molecules to the dimerized silicon (100) surface due to the importance of the surface to device fabrication. In theoretical research, slab models and cluster models have been extensively used to describe Si(100) - $2 \times 1$  surfaces [45 ~ 47]. Among these models, the cluster model has been extensively used in theoretical research of the surface since it is simple and amenable to model the

fundamental features of the surface. The smallest cluster model for the  $2 \times 1$ -reconstructed Si(100) surface is the  $Si_9H_{12}$  one-dimer cluster, which includes two surface Si atoms representing the dimer structure, four second layer silicon atoms, two third layer silicon atoms, and one fourth layer silicon atom. Although this cluster can be used to simulate the bulk feature of silicon, the one dimer cluster does not describe the surface reaction adequately [46]. In order to adequately describe the surface and minimize the computing expense, we adopt the three dimer cluster model  $Si_{21}H_{20}$ . As the energy gain per dimer for the three-dimer cluster is between 0.15-0.20eV and in agreement with the slab results to better than 0.05eV, it is possible to infer the characteristics of the Si(100)- $2 \times 1$  surface from the three-dimer cluster  $Si_{21}H_{20}$  [47]. In order to analyze the previously stated two questions, we numerically calculated the Mulliken population of the system in terms of density functional theory. The program used in the calculation is GAMESS. The base function is 6-31G\*\*. The exchange and correlation is expressed by PBELYP. Geometrical optimization has been performed on the model of silicon (100) –  $2 \times 1$  surface.

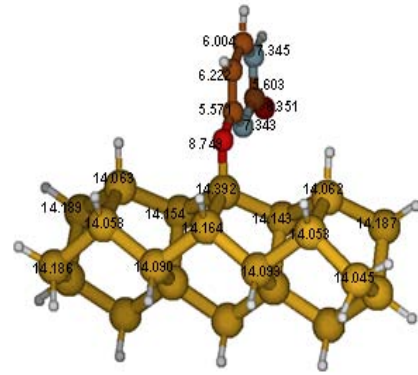
### Calculation Results and Analyses

For  $\pi$ -conjugated molecular systems to be used as conductors or semiconductors, they must retain  $\pi$ -conjugation, even after absorption onto the surface of silicon. Among the  $\pi$ -conjugated systems, benzene molecule, the simplest  $\pi$ -conjugated system, can be absorbed onto the Si (100)-  $2 \times 1$  surface by Si – C linkage. However, the formation of new Si-C bonds leads to the loss of  $\pi$ -conjugation of the system [48]. The broken of the  $\pi$ -conjugation greatly reduces the electron transport capabilities of the molecule which is the result of the localization of the electrons in the molecule. Thus, the key issue of attaching a  $\pi$ -conjugated system to the surface of silicon is to find suitable attaching mechanism to ensure the  $\pi$ -conjugation after the attachment of the molecules. Experimentally, this task can be finished using the following methods: 1). Using a sulfur atom as a tether for selective attachment of aromatic molecules to silicon (100) surface [49]; 2). Formation of a benzoimine-like conjugated structure through the absorption of benzonitrile on silicon (100) surface [50]; 3). Using Ge-covered silicon (100) surface as a tempting template and highly selective binding of styrene through cycloaddition reaction between vinyl group of styrene and an Ge = Ge dimer [51]; 4). as well as direct Si – C linkage between a polycyclic aromatic molecule and silicon (100) surface [52]. Among these techniques of binding aromatic molecules to silicon (100) surfaces, the charge distribution in the Si – C linkage and the Si – S linkage determine the electrical features of the contacts.

## Electrical characteristics of Si – S linkage



**Figure 3** Geometrical structure of the attachment of benzenethiol on the surface of silicon (100) – 2×1 surface and Milliken population of the atoms.



**Figure 4** Geometrical structure of the attachment of a Uracil on the surface of silicon (100) – 2×1 surface and Milliken population of the atoms.

Considering the attachment of benzenethiol on silicon (100) - 2×1 surface. Fig. 3 illustrates the binding structures of benzenethiol and silicon (100) - 2×1 surface [48]. It also shows the Milliken population of each atom. For an isolated sulfur atom, it has sixteen electrons. As shown by the figure, the sulfur atom has 16.30 electrons in the bonded structures. Since more electrons are located on the site of sulfur atom, the sulfur atom establishes a potential barrier between the benzene molecule and the silicon surface. In the meantime, there is depletion of electrons on the points of silicon surface and the benzene molecule that contacts the sulfur atom. The formation of the potential barrier on the sulfur atom can be understood in terms of the electronegativities of the atoms. The electronegativities of the isolated sulfur atom, carbon atom, and silicon atom are 2.58, 2.55, and 1.9, respectively. Thus, the sulfur atom attracts electrons from the silicon atom contacting to it in the binding process. On the other hand, an isolated sulfur atom and a carbon atom have almost the same electronegativity. They may form a non-polar covalent bond. However, when the sulfur atom is bonded to the surface of silicon, the scale of the electronegativity of sulfur increases as discussed before. Thus, the sulfur atom also attracts electrons from the carbon atom connecting to it and forming a polarized covalent bond, as shown by Fig.1. Because of the potential barrier formed between the benzene molecule and the surface of silicon, this type of contact is a Schottky – like contact.

## Electrical Characteristics of Si - O linkages

For Si-O linkage, we take the geometrical structure studied by Lopez et al as shown in Fig.4 {lopez}. Here, an Uracil is attached onto the silicon (100) surface through the Si - O linkage. This figure shows that the tether atom, Oxygen atom, creates an electric barrier between the molecule and the surface of silicon. Comparing the value of the Mulliken population of the tether atom with the sulfur atom in Fig. 3, we can see that the height of the barrier created by the oxygen atom is greater than that created by sulfur atom when they are used to connect the molecules with the silicon surface. Hence, the basic electrostatic characteristics of a tether atom

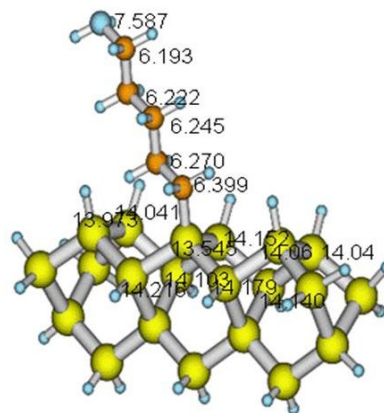
is that the greater the value of the electronegativity of the tether atom, the higher the potential barrier it creates between the organic molecules and the surface of silicon.

### Electrical Characteristics of Si – C linkages

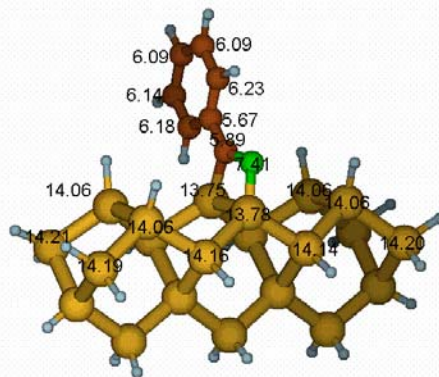
For a non-cyclical attachment as shown in Fig. 5, there are more electrons on the atom C. Therefore, there should be an electric barrier between the molecule and the surface of silicon. This electric barrier influence the sensitivity of the surface. For cyclical attachment, we consider the attachment of benzonitrile molecule onto silicon (100) -  $2 \times 1$  surface. The geometrical structure of the attachment shown by Fig. 6 has been experimentally verified [50]. Comparing to Si – S linkage, this linking structure has two advantages: 1). the carbon, nitrogen, and silicon atoms form a circularly structure. This structure is stable and can retain the  $\pi$ -conjugation of the molecule even after the molecule is absorbed onto the surface of silicon, thereby making it possible to retain the  $\pi$ -conjugation of the system. This is an important technique requirement to molecular based information processing systems; 2). There is a pathway of electrons between the molecule and the silicon surface. As we know the carbon atom, silicon atom, and nitrogen atom have six electrons, fourteen electrons, and seven electrons, respectively. As shown by Fig.6, there is electron population deficiency of the carbon atoms and silicon atoms near the attachment point. Furthermore, the Milliken populations of the atoms illustrated by Fig. 6 show that there is no potential barrier between the benzene molecule and the silicon surface. This deficiency of electron population of atoms provides a potential channel for the transfer of electrons from the molecule to the surface of silicon or from the surface of silicon to the molecule. This conduction channel is created by the difference of the electronegativities of the atoms. Here, the nitrogen atom is a key factor for its electronegativity (3.04) is much larger than those of the carbon atom and the silicon atom. Thus, the nitrogen atom attracts electrons from carbon atoms and silicon atoms. It is this attraction of electrons from carbon atoms and silicon atoms that leads to the creation of the electronic conduction channel through the surface of silicon to the molecule. Since there is no potential barrier between the molecule and the silicon surface, this type of contact is Ohmic-like contact.

### Summary

In this research, we have, in terms of density functional theory, qualitatively studied the electrostatic characteristics of the attachment of organic molecules onto silicon (100) -  $2 \times 1$  surfaces. Our numerical calculation results show that, in the case of Si - S linkage, the sulfur

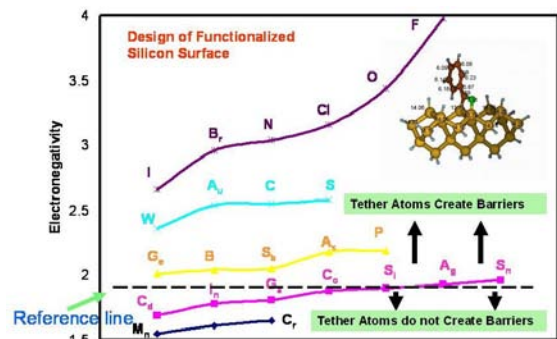


**Figure 5** Geometrical structure of the attachment of a  $(\text{CH}_2)_5\text{NH}_2$  on the surface of silicon (100) -  $2 \times 1$  surface and Milliken population of the atoms.



**Figure 6** Geometrical structure of the attachment of benzonitrile on the surface of silicon (100) -  $2 \times 1$  surface and Milliken population of the atoms.

atom establishes a potential barrier between a molecule and the surface of silicon for electrons. This type of contacts is a Schottky-like contact. This conclusion is true for Si-O linkage in addition to a higher barrier between the molecule and the silicon surface. For Si - C linkage, the molecule may be attached to the surface of silicon via a cyano group selectively binding to the surface (100) of silicon through a typical 1, 2 - dipolar cycloaddition of cyano group with a silicon dimer. Here the carbon in the cyano group does not establish a potential barrier between the molecule and the surface (100) of silicon. An electron motion channel is formed while the benzonitrile is adsorbed onto the surface of Si (100) because the electronegativity of the nitrogen atom is higher than those of carbon atoms and the silicon atoms. These results illustrate the basic rules for the design of the electrostatic characteristics of the contact between the molecules and the silicon surfaces as shown in Figure 7. The dashed line in the figure is the reference line for silicon surface. For noncyclical attachment, the tether atoms above this line have greater electronegativities than that of silicon atoms. They will create barriers between the linker molecules and the surface, which form a Schottky-like contact for electrons. Below this line, the electronegativities of the tether atoms are slightly less than that of silicon atoms. These atoms create charge traps instead of barriers between the linker molecule and the surface for electrons, which form an Ohmic-like contact. This figure also shows that silver atoms are the most electrically effective tether atoms that create neither barriers nor charge traps for electrons. An Ohmic-like contact can also be created by using a cyclical attachment as shown in Fig. 6 where the electronegativity of the stand-by atom (the nitrogen atom) is greater than those of the carbon and silicon atoms. These results suggest a way for the design of a stable and electrically effective contact between a molecule and the surface of silicon. The electrostatic characteristics of the contact can be modulated by adjusting the electronegativity of the stand-by atom in the side branch of a cyclical attachment structure. This design variation is a noteworthy and one that will have important utility in practical applications.



**Figure 7** Methodology for Design of Substrate

#### §4. Publications

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- 2). Towards Sensing Single or A Few Bio-Molecular Architectures, Peiji Zhao, Dwight Woolard, Jorge M. Seminario, Robert Trew, Journal of High Speed Electronics and Systems, 18(1), 187 - 194(2008)..
- 3). Mixed-Valence Transition-Metal Complex Based Integral Architecture for Molecular Computing, Peiji Zhao, Dwight Woolard, and Jorge M. Seminario, Journal of High Speed Electronics and Systems 16, 705(2006).

4). Mixed-Valence Transition Metal Complexes for Molecular Computing, Peiji Zhao, Dwight Woolard, and Jorge M. Seminario, 4th IEEE Conference on Nanotechnology, German, 2004

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