PHYSICS OF CARBONYL DOPED TRANSITION METAL OXIDES FOR A NON-VOLATILE MEMORY

by

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B.S., University of Colorado Colorado Springs, 2014

A thesis submitted to the Graduate Faculty of the
University of Colorado Colorado Springs
in partial fulfillment of the
requirements for the degree of
Master of Science
Department of Electrical and Computer Engineering
2019
This thesis for the Master of Science degree by

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Date: 2019-05-08
Abstract

This thesis reviews the current state of technologies used in non-volatile memory and the limitations these technologies create for memory and CPU systems. A detailed review and analysis of the physics found in electron-electron interactions in doped transition metal oxides is then provided. This analysis serves as the basis for analyzing CeRAM; a technology that relies on electron-electron interactions that has the potential to serve as a replacement for current memory systems.
Dedication

I dedicate this thesis to my parents, Dale and Susan Shoemaker, and my sister, Rachel Calvert. They provided me with endless support and encouragement while I worked on this thesis, and for that I will be forever grateful.
Acknowledgments

I wish to acknowledge and thank my advisor and professor, Dr. Carlos Araujo, for the incredible support he has given me while writing this thesis. He hired me to work with the CeRAM material his company has produced, giving me valuable insight into the world of semiconductor development, and his encouragement allowed me to write a thesis on a fascinating piece of modern technology.
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CHAPTER I

INTRODUCTION

This thesis is a study on the device physics of a new type of resistive switching non-volatile memory, called CeRAM. It will focus on the device model and the physics that drive this new memory.

Resistive switching random access memories (ReRAMs) have been researched intensively since the first decade of the twenty-first century due to its many advantages over current flash memory technology. Although ReRAM shows promise in some non Von-Neumann new computer architectures, the stochastic nature of switching due to soft breakdown of oxides hinders the widespread use of these devices. Soft-breakdown and creation of random filaments across the device leads to device failure mechanisms and there is no universal explanation of the underlying physics responsible for resistive switching. The discovery that transition metal oxides, when modified by Carbonyl (CO) "doping", creates filament free switching became a new area of study and is the focus of this thesis [1].

Metal-insulator phase transitions, the primary method of switching in this new device, are by themselves a fundamental and challenging area of condensed matter physics. These transitions involve electron-electron strong interactions or correlations. Such interactions appear at the orbital level of transition metal oxides due to incompletely filled d and f orbitals. The underlying physics causes a severe departure from the well-known band theory of metals, semiconductors, and insulators.

Switching between an insulating phase and a conductive phase solely by the quantum effect of orbital occupation has been named "Correlated-Electron Switching". Non-volatile memories of this type are called CeRAMs (Correlated-Electron Random Access Memories).

Semiconductors and "band insulators" (eg. SiO\textsubscript{2}) lack strong electron-electron interactions. Band gaps in these materials arrive solely by electron-lattice interactions. Such interactions allow for plane-wave like electron "extended states" which form the well-known conduction and valence bands that extend throughout these materials. Such well-known "band theory" models are not able to explain CeRAM device physics.
Strongly-correlated bands are narrow bands that induce electron-electron correlation and electron localization due to the strong Coulomb local electrostatic energy. The energy gap in these materials is not due to "extended states" but to local intra-cell Coulomb repulsion in doubly occupied orbitals. A case in point is NiO. Although later discovered to be a more complex "charge transfer Mott insulator", the fundamental appearance of a charge gap due to the local charge disproportionation $Ni^{\text{2+}}O + Ni^{\text{2+}}O \rightarrow Ni^{\text{3+}}O + Ni^{\text{1+}}O$, or in atomic orbital $3d^8 + 3d^8 \rightarrow 3d^7 + 3d^9$, is responsible for a gap due to the orbital driven band split from $3d^8$ to $3d^7$ and $3d^9$. Thus the charge induced gap ($E_{\text{GAP}} = E_{3d^9} - E_{3d^7}$) is a consequence of the Coulomb energy $U = \frac{q^2}{4\pi\varepsilon_0 r}$, and the narrow kinetic energy band. Thus, $E_{\text{GAP}} = U - W$, where $W$ is the width of the upper and lower bands.

CeRAM works because $U - W$ is modified by a somewhat complex local adjustment of the metal electronegativity via the Carbonyl double effect of donating electrons to the metal (via sigma bonds), while yet receiving from the metal charge back-donation to the empty CO molecular orbitals. This reduces the gap from 4eV to 0.6eV and allows independently controlling p-type conductivity as the Fermi-level drops due to back-donation. The current-voltage characteristics of CeRAM and the fundamental physical model of Mott Switching are the central concerns of this thesis.

Chapter II is a review of the state-of-the-art of ReRAMs. It describes some of the types of ReRAM currently being studied and points out the problems of filamentary resistive switching. Chapter III introduces the quantum physics of electrons and concludes with the presentation of a Hamiltonian that describes the minimal aspects of electronic strong correlation (the Hubbard Hamiltonian). The simplified ultra-narrow band version is of the Hubbard model is modified to incorporate the effective potential ($U_{\text{eff}}$) which incorporates electron screening. In chapter IV the device model shows that screening by injected hot electrons (and consequently electron density), is solely responsible for the insulator to metal transition (typically at a voltage of $V_{\text{set}} \approx |\phi_n - \frac{U}{q}|$), where $\phi_n$ is the electron work function. The metal to insulator transition is accomplished by hole-injection / electron extraction in the anode region and culminates when $\delta_p \approx \delta_n$, i.e. excess electrons no longer screen the doubly occupied orbitals. This is accomplished at $V_{\text{reset}} \approx \frac{U}{q}$. In both cases $U = U_{\text{eff}}$ where screening is the dominant mechanism via Mott’s use of the Yakawa potential [2].

Chapter V shows the CeRAM device model, the experimental data, and the efficacy of the physics based device model to extend to the other co-doped transition metal oxides and rare-earth
perovskites, namely \( NiO \) and \( YT\text{i}O_3 \). Chapter VI concludes with an overview of CeRAM and a discussion of areas for future research.
CHAPTER II
LIMITATIONS OF NANOIONIC RERAM SYSTEMS

Resistive Memories

Resistive switching random access memory (ReRAM) is a memory technology that could serve as a replacement for the flash memory currently used for nonvolatile data storage [3]. ReRAM systems have some advantages over flash memory, such as faster read and write speeds, nondestructive reading, and it can be scaled down to smaller sizes than current flash memory systems. While it goes outside the scope of this thesis, readers desiring a more detailed review of this subject will find that [3] is an authoritative compendium of over 4,000 papers published in the last 12 years.

These memories rely on changing the electrical resistance of a memory cell to store binary data as a ‘1’ or ‘0’. In general resistive memories utilize the "filament model" of a metal-insulator-metal (MIM) cell where the resistance changes normally occur in thin films near one or both of the interface regions by the electrodes in a ReRAM cell. With the filament model, a memory cell undergoes an initial electroforming event where a large amount of current is run through the cell, creating a single conductive path between the two electrodes of a cell. This results in the switching event taking place near the electrodes, where the tip of the filament will either be extended to touch the electrode opposite of its base, or that filament being broken to disconnect the electrodes. ReRAM memories are normally classified based on the method used to change the electrical resistance of the cell. These switching methods are primarily driven by thermal, magnetic, or electrical effects.

Thermal energy drives the changes in Phase Change Memories (PCM), which rely on amorphous-crystallization materials to create a ReRAM cell. The state of the cell is altered using Joule heating to shift the material between a crystallized conducting state and a non-conducting amorphous state. Defect and interface effects of the crystalline material at the electrodes create contacts across the cell. A brief high-temperature state is used to break the crystalline material into an amorphous state to ‘reset’ the device, while a longer low-temperature electrical pulse is used to ‘set’ the device to a conducting state.

An example of electrically-driven systems is Conductive Bridge Memories (CBM), which use
reduction-oxidation (redox) reactions and ionic transports to serve as a method of switching for a memory cell. These memories create a channel of mobile ions, such as silver or copper, in a solid electrolytic medium. If the channel is not filled the cell is in a high resistance state. When the ions have filled the channel and created a filament the cell will shift to a low resistance state.

Magnetic polarization can serve as the basis for ReRAM with Spin Transfer Torque (STT) systems. STT systems use polarized currents to change the magnetic polarity of a cell. Spin-based interactions can then limit the flow of current through the cell [4].

Limits of ReRAM

There are limitations to ReRAM systems that have prevented their large-scale adoption by the market. The first barrier to commercial adoption of PCMs is the high current densities needed to create temperatures sufficient to trigger the switching mechanism in the memory cell. This means that the thermally induced phase change of the storage medium requires temperatures that will lead to the resistance of the cell changing over time. This in turn means the voltage needed to set or reset a cell will also drift, eventually leading to the memory cell becoming unresponsive to the voltage applied to it.

The second limitation of phase-change based ReRAMs is due to the filament model used to create the switching effect in such systems. Unfortunately this leads to serious concerns regarding the endurance of ReRAM systems. The repeated forming and breaking of the filaments can lead to a filament permanently connecting the electrodes if the cell is exposed to excessive voltage, high temperatures, or through the device simply wearing out. This will result in the filament short-circuiting the ReRAM cell, rendering it useless.

CeRAM does not suffer from these limitations, as the phase change occurs on the quantum level. The physical material composing the medium of the cell is not altered, and therefore it has the possibility to serve as a replacement of flash and other non-volatile memory memory systems [5].
CHAPTER III
THE PHYSICS OF STRONGLY CORRELATED ELECTRON MATERIALS

Introduction - A Historical Perspective

In the early 1930’s, Bloch and Wilson created what is known as the "Band Theory" [6] of solids. This theory is still the standard model of the classification of the electronic properties of materials. For example, as shown in 3.1, materials are classified as metals (3.1a) if the empty conduction band and the full valence band overlap at the Fermi level ($E_F$). The Fermi energy level describes the highest energy level or the chemical potential ($U$) of the electrons at zero temperature. Figure 3.1c shows that insulators are materials where the separation between the valence band (full) and conduction band (empty) is very wide (larger than 3eV) and the Fermi level is located within this band gap ($E_G$).

![Energy bands in a metal, semiconductor, and insulator.](image)

Since conductivity "$G$" is defined as the free electrons for energies $E >> E_F$, the density of
states (DOS(E)) - the number of electrons per unit of energy per volume, or

\[ G = q^2 D_m DOS(E = E_F), \]  

(3.1)

where \( q \) = the elemental charge and \( D_m \) = the diffusion coefficient of electrons [7]. \( G \) becomes extremely small (\( G \to 0 \)) in an insulator, since within the gap there are no impurity (doping) states which could add carriers near the Fermi level.

In the case of semiconductors, the gap is smaller than in insulators. In 3.1(b), we can see that a material such as silicon, where the undoped (no impurities) Fermi level is set at the middle of the gap (\( E_F \) by definition is then called \( E_i \), the intrinsic Fermi level) is still unable to conduct with the technology that would move the Fermi level towards the conduction band (n-type) or the valence band (p-type). Figure 3.2 show an n-type (3.2a) and p-type (3.2b) semiconductor [8].

![Diagram of Fermi levels in n- and p-type semiconductors]

Figure 3.2: The effect of doping on the Fermi level in n- and p-type semiconductors.

In what follows, the basic theory used for the calculation of DOS is described in order to clarify the difference between the "Band Theory" classification and the violation of this theory in the vast majority of the transition metal oxides (TMOs).

It was as early as 1937 that the discovery this major band theory violation was shown in the famous paper by Werner and de Voer [9]. The discussion between Sir Nevill Francis Mott and Peierls about the origin of this discrepancy became a short note in the same conference proceedings [10]. It was in 1959 that Mott published the seminal paper that showed that the local screening potential could explain why an insulator could go through an insulator-to-metal transition [11]. In
1963, John Hubbard extended the Mott model to a full quantum mechanical model by ignoring the electron-lattice interaction. In the "Hubbard Hamiltonian" [12] only the local electrostatic repulsion \( (U) \) is important for the phase transition to occur. This explained the Mott model by showing that the ratio of the kinetic energy to potential energy \( (u) \), was controlled by the orbitals that would be doubly occupied (repulsing) due to a change in oxidation number. The double occupation of the orbitals would split the single energy band as shown in figure 3.3.

![Figure 3.3: Energy bands in an insulating state.](image)

In the case of a single atom \( W = 0 \) and \( E_G = U \). Or as in NiO:

\[
\text{Ni}^{+2}O + \text{Ni}^{+2}O \rightarrow \text{Ni}^{+3}O + \text{Ni}^{+1}O.
\] (3.2)

When the same material changes oxidation numbers (or more specifically "coordination number" - i.e. the number of cations/anions from a unit cell) they are called coordination compounds. The case of NiO is a classic \( MO_6 \) coordination compound where Ni is \( M \) and six oxygen anions surround the metal as shown in figure 3.4 below.
Then the chemical formula NiO comes from $Ni + 6(\frac{1}{6}O) = NiO$ and reflects the octahedral coordination and $Ni^{2+}O^{2-}$ is in charge equilibrium with the net charge of zero.

Perovskites such as $YNiO_4$ or $YTiO_3$ are Mott insulators which have similar octahedral coordination (although in a $ABO_4$ perovskite cell).

A key focus of this thesis is to show that the device model for $NiO$ CeRAMs is universal and can be used in other materials such as $YTiO_4$. However, the technology of carbonyl (CO) doping was the discovery that separated a typical ReRAM with filaments from a "Mott Switch" (thus, a quantum driven mechanism) as done in CeRAM [13].

**Introduction - The Physical Basis**

The Schrödinger’s equation for a metal where $h_0$ yields:

$$h_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x).$$

In an ideal free electron model, where there are no interactions, the potential term $V(x)$ will be zero, reflecting the lack of interactions. The Jellium model is a more accurate model that introduces kinetic energy into the electrons. This energy comes from the positive background ions in the
medium of the memory cell, but the Jellium model assumes that this positive charge is evenly distributed across the medium. Semiconductors do not fit this model as the electrons are not totally free in such materials. The periodic lattice potential, where $V(x + a) = V(x)$, yields the gaps found in the band insulators of semiconductors. Mott insulators focus on a highly localized potential $U$. This gives a system with a Hamiltonian of

$$H = H_0 + V(x) \to H = KE + U.$$ \hspace{1cm} (3.4)

This $U$ value will switch between multiple states based on the Thomas-Fermi screening length, $(\lambda_{TF})$. When the positive ions in a system are fully screened, the radius of the electron orbits around a central ion will be on the order of the Bohr radius, $a_B$; this yields a $U_0$ value of

$$U_0 = \frac{q^2}{4\pi\varepsilon_0 a_B} = \frac{q^2}{4\pi\varepsilon_0 a_B} \hspace{1cm} (3.5)$$

When the ions are only partially screened, this leads to an effective $U$ value of

$$U_{\text{eff}} = U_0 e^{-\lambda_{TF} r} = \frac{q^2}{4\pi\varepsilon_0 r} e^{-\lambda_{TF} r} \hspace{1cm} (3.6)$$

In the fully screened state the material acts like a metal and the system is in a conductive state. When partially screened the material will serve as an insulator.

![Figure 3.5: Ion screened with excess electrons](image1.png)

![Figure 3.6: Ion unscreened by electrons](image2.png)

Figure 3.5 shows that when the background ions are fully screened, the cell acts as a metal where
electrons can flow freely through the cell. When the background ions are only partially screened (as seen in figure 3.6) the Thomas-Fermi screening length is much larger than the Bohr radius $\lambda_{TF} > a_B$. This means the positive ions will interrupt the flow of electrons and the system will show insulating behavior.

![Figure 3.7: Current density to voltage graph of an ideal CeRAM system.](image)

Unlike most materials CeRAM has different points on its J-V graph when the system changes from the metal to insulating phase (MI transition) and when it shifts from the insulator to metal phase (IM transition). The $J_{On} \rightarrow J_{Off}$ point of the M→I transition can be found with the equation

$$J_{OnMax} = q \partial p v_f$$  \hspace{1cm} (3.7)

where $\partial p \approx \partial n$. At this point of the graph the number of injected positive ions equals the injected number of electrons. In this state the positive ions are not screened by electrons, leading to an insulating state. The I→M transition can be found by locating the compliance current at

$$J_{Comp} = q n_c v_f$$  \hspace{1cm} (3.8)
where the critical electron density \( n_c \) is the number of electrons that have been injected plus the electrons due to doping: \( n_c = \partial n + n_{doping} \). It should be noted that this requires strong negative doping of the material, such that \( n_0 \ll \partial n \). This means the transition point can be found at

\[
M = \frac{J_{Comp}}{qv_f}.
\] (3.9)

The critical electron density is a key value needed to understand the behavior of a CeRAM cell. It determines the set and reset voltages which are essential to the cell’s operation. At the set point the critical electron density is found with \( n_c = \partial n_{\text{Injected}} + n_0 \). At the reset point the critical density is \( n_c \approx n_0 \), meaning the injected electrons \( \partial n_{\text{Injected}} = 0 \) and \( \partial n \approx \partial p \). The critical electron density \( n_c \) is inversely proportional to the Thomas-Fermi screening length

\[
\lambda_{TF} \propto \frac{1}{n_c}.
\] (3.10)

Beginning with a description of the electron density (electron gas) and its relationship to electron-electron interactions, we will describe step-by-step the underlying physics of electron interaction and the CeRAM model.

The first model is the hypothetical "free electron" model which, in some cases, can be used to describe a metal such as copper. The free electron gas ignores all interactions such as electron-lattice, electron-electron "weak Coulomb interactions" and "strong electron interactions" which are responsible for the insulating state of Mott insulators and CeRAM. In the Schrödinger equation the Hamiltonian represents the 'model' of a system. Thus, for a general Schrödinger equation

\[
H|\Psi\rangle = E|\Psi\rangle
\] (3.11)

where \( |\Psi\rangle \) is the "ket" state vector which exists in a Hilbert space. Since \( \langle\Psi| = |\Psi\rangle^* \), the dual space contains the complex conjugate of \( |\Psi\rangle \). The wave function, following the Dirac notation, has two types of representation; 'Space Representation':

\[
\langle x|\Psi\rangle = \Psi(x)
\] (3.12)
and 'Momentum Representation':

$$\langle k | \Psi \rangle = \Psi(k)$$ (3.13)

where \( \bar{p} = \hbar \bar{k} \) is the quantum mechanical average momentum. \( \hbar = \text{Planck's constant} / 2\pi \).

\( \Psi(x) \) and \( \Psi(k) \) form Fourier transform pairs with kernel \( \langle \vec{x} | \vec{k} \rangle = \text{exp}(-i\vec{k} \cdot \vec{x}) \). Here \( \vec{x} \) is a 3-D space vector and \( \vec{k} \) is the momentum parameter \( \vec{k} = \frac{\vec{p}}{\hbar} \).

The Hamiltonian in classical dynamics incorporates the kinetic energy (T) and the potential (V). Thus,

$$H_{\text{Classical}} = T + V = \frac{p^2}{2m} + V.$$ (3.14)

In the quantum description, \( \bar{p} \) is a quantum operator \( \bar{p}_{op} = i\hbar \nabla_k \). In 1-D this is \( \bar{p}_{op} = i\hbar \frac{d}{dx} \). Thus,

$$H_{\text{Quantum}} = \frac{\bar{p}_{op}^2}{2m} + V = \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right] \Psi.$$ (3.15)

The wave operation is

$$H_{op} \Psi(x) = E \Psi(x),$$ (3.16)

where \( H_{op} = H_{\text{Quantum}} \).

In the case of the electron gas at high electron density \( n = \frac{N_e}{v}, \) where \( N_e = \text{number of electrons} \) and \( v = \text{volume} \) it is possible to define characteristic parameters of the electron gas (ignoring the electron-lattice interaction). One starts with

$$H = T_0 + V_0$$ (3.17)

with \( T_0 = \frac{\hbar^2}{2m r_0^2} \) where \( r_0 \) is the effective radius of an electron. Thus, the volume of an electron is

$$\frac{4\pi}{3} r_0^3 = \frac{v}{N_e} = \frac{1}{n}. \quad (3.18)$$

Mott used this semi-classical concept to develop his 1958-59 [10] model for metal-insulator transitions (see below). \( V_0 \) is the Coulomb potential energy at a position \( \vec{x} = r_0 \). Thus,

$$V_0 = \frac{q^2}{4\pi \epsilon_0 r_0} = U. \quad (3.19)$$
Mott’s criteria for metal-insulator transition is found from \( \frac{4}{3} r_0^3 = n^{-1} \), which yields the relationship between electron density and electron-electron distance (wave overlap). Thus

\[
n^{\frac{1}{3}} r_0 = 0.26
\]  

(3.20)

means that \( r_0 \), which could also be the contact distance between two electrons in the valence shell can be used as the first order parameter to indicate a Mott transition. Using the Slater parameter \( r_s = \frac{a_0}{a_B} \) where \( a_B \) is the Bohr Radius \( (a_B = \frac{4\pi\varepsilon_0\hbar^2}{mc^2}) \) we can express the Mott criteria in units of \( a_B \),

\[
n^{\frac{1}{3}} (r_s a_B) \approx 0.26.
\]  

(3.21)

This remarkably simple equation is rather accurate [2] and \( r_s \) can be linked to the electron density as

\[
r_s = \frac{r_0}{a_B} = \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} n^{-\frac{1}{3}} \frac{1}{a_B}.
\]  

(3.22)

Electrons in solids are in constant competition between being free to move (high kinetic energy) or localized by being captured in Coulomb Potential. It can be shown that

\[
r_s = \frac{\text{PotentialEnergy}}{\text{KineticEnergy}}
\]  

(3.23)

to a first order, thus

\[
r_s = \frac{q^2}{4\pi\varepsilon_0 r_0} \frac{\hbar^2}{mr_0}
\]  

(3.24)

Since

\[
r_s = \frac{1}{a_B n^{\frac{1}{3}}} \rightarrow 0.26,
\]  

(3.25)

the correlation energy and the cohesive energy can also be calculated as a function of \( r_s \).

For high electron densities, \( r_s \) approaches the Bohr radius. This means that electrons completely screen the positively charged ion cores in a metal. Thus, in the metal phase the kinetic energy dominates. On the reverse, lower electron density leads to a high value of \( r_s \) such that the electron can be captured (a bound state) in the extended and under-screened core potential. In this case \( V_0 \) dominates. (e.g. for a metal \( 2 < r_s \leq 6 \)).
The CeRAM storage cell switches between these two states by starting in a p-type conductive phase and controlling the population of screening electrons. The quantum Hamiltonian for describing the phase transitions that in CeRAM cells are induced by electron screening becomes the fundamental physical model which is used here for a device model. In comparison with silicon devices, which due to the low electron-electron Coulomb interaction (via doping, an electron is typically 10,000\(r_0\) away from another), transition metal oxides (TMOs) have \(V_0\) of 4eV - 10eV and \(U_{eff} \gg W\) (the band width is related to kinetic energy).

**The Jellium Model**

One of the oldest models for understanding the structure of the atom within the framework of quantum mechanics is the Jellium model; also known as the Uniform Electron Gas or Homogeneous Electron Gas model. This model portrays the positive charge of the nuclei in a solid as a uniform background charge, and electrons are treated as if they have an equal occupation probability across the material. This allows for the effects of these charges to be calculated without taking into account the effect of any lattice structures the solid may contain. This is an effective model for describing simple metals, provided four assumptions are made. First, there are \(N_e\) electrons within the volume \(V = L^3\), which interact via Coulomb interaction

\[
H_{ee} = \frac{e^2}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.
\]  

(3.26)

Second, the ions have a single positive charge, thus

\[
N_e = N_i = N
\]  

(3.27)

where \(N_e\) is the number of electrons and \(N_i\) is the number of ions.

Third, the ions are homogeneous, which guarantees charge neutrality and a constant lattice potential. This turns the Bloch functions into plane waves as shown in (3.28):

\[
\psi_{k\sigma}(\mathbf{r}) \Rightarrow \frac{1}{\sqrt{V}} e^{i \mathbf{k} \cdot \mathbf{r}} \chi_{\sigma}
\]  

(3.28)

where \(\chi_{\sigma} = 0, 1 = \uparrow, \downarrow\).
Finally, periodic boundary conditions for $V$ give rise to discrete wave numbers

$$k = \frac{2\pi}{L} (n_x, n_y, n_z) \quad (3.29)$$

These conditions lead to a Hamiltonian for the system which contains three parts

$$H = H_e + H_+ + H_{e+} \quad (3.30)$$

Here, $H_e$ is the sum of the kinetic energy and the Coulomb interactions of the electrons, $H_+$ is the effect of the homogeneous positive charge, and $H_{e+}$ describes the interaction of the electrons with the positive background charge.

To better analyze the system, it is useful to describe the interactions of the electrons with the positive ion background. For a single particle, this interaction can be found by adding the lattice potentials $\hat{V}$ for the electron

$$H_{ei}^{(0)} = \sum_{i=1}^{N_e} \hat{V}(r_i). \quad (3.31)$$

It is therefore necessary to solve the eigenvalue equation

$$h_0 \psi_k(r) = \varepsilon(k) \psi_k(r). \quad (3.32)$$

In this equation $\psi_k(r)$ is a Bloch function with a Bloch energy of $\varepsilon(k)$. $k$ is a wave vector within the first Brillouin zone, and the operator $h_0$ is defined as

$$h_0 = \frac{p^2}{2m} + \hat{V}(r_i). \quad (3.33)$$

Following Nolting [14], solving this eigenfunction equation requires the definition of creation and annihilation operators for the Bloch electron, which are $a_{k\sigma}$ and $a_{k\sigma}^\dagger$ respectively. The term $\sigma$ denotes the spin of the electron. With a Bloch state represented as $|k\sigma\rangle$, the Bloch energy can be calculated as

$$\langle k\sigma| h_0 |k'\sigma' \rangle = \varepsilon(k') \langle k\sigma | k'\sigma' \rangle = \varepsilon(k) \delta_{kk'} \delta_{\sigma\sigma'}. \quad (3.34)$$
As $|\mathbf{k}\sigma\rangle$ is an eigenstate of $h_0$, the Hamiltonian of a non-interacting system is

$$H_0 = \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} = \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) n_{\mathbf{k}\sigma}$$  \hspace{1cm} (3.35)

It should be noted that for a free electron the Bloch operators for creation and annihilation fulfill the fundamental commutation relations

$$[a_{\mathbf{k}\sigma}, a_{\mathbf{k}'\sigma'}]^+ = [a_{\mathbf{k}\sigma}^+, a_{\mathbf{k}'\sigma'}] = 0,$$  \hspace{1cm} (3.36)

$$[a_{\mathbf{k}\sigma}, a_{\mathbf{k}'\sigma'}^+] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma'}.$$  \hspace{1cm} (3.37)

This leads to the field operators for $H_0$

$$\hat{\psi}^+_{\sigma}(\mathbf{r}), \hat{\psi}_{\sigma}(\mathbf{r})$$

These field operators serve as second-order creation and annihilation operators for the energy fields held by the particles.

Wannier functions are one way to represent a lattice. A useful feature of this representation is the relatively strong concentration of particles around each lattice position $\mathbf{R}_i$, as seen in fig. 3.8. The notation for the Wannier state is:

$$|i\sigma\rangle \iff \text{Wannier state}, \hspace{1cm} (3.39)$$

$$\langle \mathbf{r}|i\sigma\rangle = \omega_\sigma(\mathbf{r} - \mathbf{R}_i)$$  \hspace{1cm} (3.40)

$$a_{i\sigma}^+ \ (a_{i\sigma}) : \text{Creation (annihilation) operator for an electron in the Wannier state at the site } \mathbf{R}_i \hspace{1cm} (3.41)$$

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Using this notation, the second order Hamiltonian term $H_0$ becomes

$$H_0 = \sum_{ij\sigma} T_{ij}a_{i\sigma}^+a_{j\sigma},$$

(3.42)

This describes an electron with spin $\theta$ being annihilated at site $R_j$ and then created at site $R_i$. This leads to the ‘hopping integral’ $T_{ij}$, defined as:

$$T_{ij} = \frac{1}{N_i} \sum_k \epsilon(k)e^{ik(R_i-R_j)}.$$  

(3.43)

The relationship between the Bloch and Wannier operators is

$$a_{i\sigma} = \frac{1}{\sqrt{N_i}} \sum_k 1_{BZ}\epsilon(k) e^{ikR_i} a_{k\sigma},$$

(3.44)

$$a_{k\sigma} = \frac{1}{\sqrt{N_i}} \sum_{i=1}^{N_i} e^{-ikR_i} a_{i\sigma}. $$

(3.45)

A complete Hamiltonian for the Jellium model is

$$H = \sum_k \epsilon_0(k)a_k^+a_k + \frac{1}{2} \sum_{\substack{k, p, q \sigma, \sigma' \neq \sigma}} V_0(q) a_{k+q\sigma}^+ a_{k+q\sigma} a_{p-q\sigma}^+ a_{p\sigma'} a_{k\sigma}. $$

(3.46)

To simplify this equation, the terms $a_k^+a_k$ can be rewritten as $n_k$, the term $a_{k+q\sigma}^+a_{k+q\sigma}$ can be represented as $n_{k+q}$, and the term $a_{p-q\sigma}^+a_{p\sigma'} a_{k\sigma}$ is represented with $n_{k\sigma}$. The voltage component of the equation can be represented as

$$V_0(q) = \frac{e^2}{4\pi\epsilon_0 q^2}.$$  

(3.47)
which has a Fourier transform of

\[ V_0(r) = \frac{e^2}{4\pi \varepsilon_0 r_0} = U_{\text{fixed}} \]  

(3.48)

This leads to

\[ V_1(q) = \frac{e^2}{4\pi \varepsilon_0 (q^2 + \frac{1}{\lambda_{\text{TF}}})} = \frac{e^2}{4\pi \varepsilon_0 (q^2 + K_{\text{TF}}^2)} \]  

(3.49)

### The Ultra-Narrow Band Hubbard Model

A major limitation of the Jellium model is that it only provides a useful approximation for electrons in materials with a broad energy band. In a narrow energy band electrons have less mobility and have a substantially higher probability of being near to the ions at the lattice points of a crystal. This means that the Bloch waves cannot be considered plane waves, and a better model is needed for accurately predicting the behavior of electrons. This is provided by the narrow-band Hubbard model which is derived from the tight-binding approximation.

With the tight binding model electrons are considered to be closely bound to their atomic core, and are assumed to have minimal interactions with the electrons of nearby atoms. With low electron mobility and a strong lattice potential \( \hat{V}(r) \), the atomic Hamiltonian can represented as

\[ H_{\text{at}} = \sum_{i=1}^{N_i} h_{\text{at}}^{(i)}. \]  

(3.50)

Here, the sum of the Hamiltonians for the individual atoms \( h_{\text{at}} \) should provide a reasonable description of the material. Adding in a correction factor for the lattice potential yields a non-interacting Hamiltonian

\[ h_0 = h_{\text{at}} + \hat{V}_1(r). \]  

(3.51)

The correction factor should be small near the lattice ions but relatively large in the areas where atomic waveforms overlap. However, it needs to be noted that in the intermediate regions the atomic wavefunctions \( \psi_n \) will be nearly zero.

In the second quantization, the non-interacting Hamiltonian takes the same form as (3.42). The hopping integral is also displayed in the same form as in (3.43). When converted to real space, the
electron-electron Hamiltonian will show the force of the interactions as

\[ H_{ee} = \frac{1}{2} \sum_{ijkl, \sigma, \sigma'} v(ij; kl) a_{i\sigma}^+ a_{j\sigma'}^+ a_{i\sigma'} a_{k\sigma}. \]  

(3.52)

Due to the small overlap of the atomic wavefunctions, the inter-atomic matrix element

\[ U = v(ii; ii) \]  

(3.53)

dominates. This allowed Hubbard to simplify the Hamiltonian to

\[ H_{ee} = \sum_{ij} T_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} \sum_{i, \sigma} U n_i \hat{n}_{i-\sigma}. \]  

(3.54)

This makes the Hubbard model a very simple model that still allows for the discussion of the electronic properties of transition metals, band magnetism, general principles of statistical mechanics, high temperature superconductors, and - most importantly for this paper - Mott metal-insulator transitions.

A special exactly solvable case of the Hubbard model is a useful starting point for this analysis. This special case is an infinitely narrow band, with a Hamiltonian of

\[ H = \sum_{ij, \sigma} (T_{ij} - \mu \delta_{ij}) a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} U \sum_{i, \sigma} n_{i\sigma} n_{i-\sigma} \]  

(3.55)

Finally, make use of the relation (which holds for Fermions)

\[ n_{i\sigma}^2 = n_{i-\sigma} \]  

(3.56)

Combining all of these components yields an equation of motion:

\[ (E + \mu - U) \Gamma_{ii, j\sigma}(E) =  
\]

\[ = \hbar \delta_{ij} (n_{i-\sigma}) + \sum_{m} T_{im} \left\{ \Gamma_{im, j\sigma}(E) + \Gamma_{im, j\sigma}(E) + \Gamma_{mii, j\sigma}(E) \right\} \]  

(3.58)

This equation results in an infinite series of \( \Gamma \) functions, but beyond the first \( \Gamma \) the effect of these
functions is negligible. By dropping the other functions, the Dyson approximation will allow us to consider only first order interactions. In the special case of an infinitely narrow Dyson energy band, this 'one-atom' model simplifies the \( \varepsilon(k) \equiv T_0 \) relationship to

\[
\varepsilon(k) \equiv T_0 \iff T_{ij} = T_0 \delta_{ij}
\]  

(3.59)

With this equality, the equation of motion (3.57) can be simplified to

\[
(E + \mu - U - T_0)G_{\alpha ii\sigma}^0(E) = \hbar \delta_{ij} \langle n_{-\sigma} \rangle.
\]

(3.60)

Since the ions in a crystalline substance are periodic, the value of the number operator is independent of the lattice site. Taking the solution of the previous equation into the one electron Green’s function (3.57) yields

\[
G_{\alpha ii\sigma}^{ret} = \frac{1 - \langle n_{-\sigma} \rangle}{E - (T_0 - \mu) + i0^+} + \frac{\hbar \langle n_{-\sigma} \rangle}{E - (T_0 + U - \mu) + i0^+}
\]

(3.61)

This means that the retarded Green’s function has two poles that could be excitation energies for the system, which correspond to conductive and insulating states in the cell. When \( n_{-\sigma} = 1 \), the system is in an insulating state, and when \( n_{-\sigma} = 0 \) the system is in a metal or conductive state. These poles are located at

\[
E_{1\sigma} = T_0 - \mu = E_{1-\sigma}
\]

(3.62)

\[
E_{2\sigma} = T_0 + U - \mu = E_{2-\sigma}
\]

(3.63)

Due to the Coulomb interactions in the system, the \( T_0 \) level is split into two quasi-particles with the labels \( E_{1\sigma} \) and \( E_{2\sigma} \); these quasi-particles are spin-independent. Next, the spectral density function can be computed from the retarded Green’s function. The alpha components are the spectral weights found to be

\[
\alpha_{1\sigma} = 1 - \langle n_{-\sigma} \rangle; \quad \alpha_{2\sigma} = \langle n_{-\sigma} \rangle
\]

(3.64)

These represent the probability that an electron \( \sigma \) will encounter an electron \( (-\sigma) \) at the location \( \alpha_{2\sigma} \) or an empty orbital at the site \( \langle \alpha_{1\sigma} \rangle \). In the case that the electron encounters an electron at the
site \( \alpha_{2d} \) it must overcome the Coulomb interaction \( U \).

The quasi-particle density of states has two infinitely narrow bands. The first is a lower, degenerate band at \( T_0 \) and the second is the upper band at \( T_0 + U \). These represent the \( d^7 \) and \( d^9 \) orbitals for the lattice ions respectively.

![Figure 3.9: DOS splitting at \( T_0 - \mu \) and \( T_0 + U - \mu \).](image)

\[
\begin{align*}
E - \mu + U & \quad \text{at } T_0 - \mu \\
E & \quad \text{at } T_0 \\
E - \mu & \quad \text{at } T_0 + U - \mu
\end{align*}
\]

Figure 3.9: DOS splitting at \( T_0 - \mu \) and \( T_0 + U - \mu \).

![Figure 3.10: Energy bands for \( d^7 \) and \( d^9 \) orbitals, centered on \( \mu \) and separated by the energy gap \( U \).](image)

\[
\begin{align*}
E_{3d^9} &= E_{3d^7} + U - \mu \\
E_{3d^7} - \mu
\end{align*}
\]

Figure 3.10: Energy bands for \( d^7 \) and \( d^9 \) orbitals, centered on \( \mu \) and separated by the energy gap \( U \).

As described above, this chapter reviews the progression of electron gas models from free electron, the electron-electron and electron-positive ions (the Jellium model of a metal), the tight binding model (free electrons that can jump from lattice site to lattice site), the Hubbard model (single band with strong \( V_0 \equiv U \)) and finally the ultra-thin band Hubbard model. The quantum model is used in Chapter IV to describe the switching mechanisms of a CeRAM storage cell as the electron density is increased or decreased via carrier injection from the electrodes.
CHAPTER IV
THE PHYSICS OF CERAM DEVICES

Introduction

In general, the electrical current can be described by \( J = qnv \) where \( n \) is the electron density, \( q \) is the elementary charge of the electron, and \( v \) is the electron velocity. If a band model is considered, the velocity term has to be described by the electron velocity in nth band and it is related to the quantum momentum \( p = \hbar k \). Thus a conducting electron will conduct in a k-based band index or n-band considering \( k = n_1k_x + n_2k_y + n_3k_z \). Also, where \( n_i = n \), will have a velocity over every k-direction and quantized with a k-space density of

\[
k = \frac{\text{Volume}}{(2\pi)^3}
\]

(4.1)
as presented in chapter 3 when discussing the Jellium Model. Thus \( J(DOS) \) since velocity in the free electron model with energy dispersion of \( E_k = \frac{\hbar^2 k^2}{2m} \) where \( k = |k| \) is

\[
V = \frac{1}{\hbar} \frac{\partial E}{\partial k}
\]

(4.2)

Thus, over all k-bands (momentum bands), the current can be the integral over k of the velocities normalized by volume

\[
J = q^2 \int \frac{1}{\hbar} \frac{\partial E}{\partial k} \frac{\partial k}{(2\pi)^3}
\]

(4.3)

where \( q = -e \). The ‘2’ term is due to spin degeneracy, \( \frac{1}{\hbar} dE d\mathbf{k} \) is the velocity, \( \frac{\partial k}{(2\pi)^3} \) is the number of electron states in momentum representation per unit value. A transformation of \( d\mathbf{k} \) to polar coordinates in the \( k_x, k_y, k_z \) space makes it easier to calculate the current. Thus let \( d\mathbf{k} = 4\pi k^2 d\mathbf{k} \) where \( \mathbf{k} = k \). Then

\[
J = -e^2 \int \frac{1}{\hbar} \frac{\partial E}{\partial k}.
\]

(4.4)

Since \( \frac{\partial E}{\partial k} = \frac{\hbar k}{m} \), then

\[
J = -e^2 \int \frac{\hbar k^2}{m} 4\pi k^2 d\mathbf{k}.
\]

(4.5)
Since the current in a memory cell is applied along only one axis, the term \( J \) can be simplified with \( J = J_z \). Taking all directions into account, the equation can then be written as

\[
J_z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} -e v_z f d p_x d p_y d p_z \\
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} -\frac{e}{m} p_z (f - f_0) d p_x d p_y d p_z. \tag{4.6}
\]

For simplicity, let \( p = \hbar k \) be the integrating variable, and also have \( p \) such that \( p^2 = p_x^2 + p_y^2 + p_z^2 \), as in \( k^2 = k_x^2 + k_y^2 + k_z^2 \). Where \( k_i \) is the \( n_i \) k-vector of \( i \). Thus the current can be written as

\[
J = -\frac{2e}{(2\pi)^3} \frac{\hbar^2}{m} 4\pi k^3 d k \tag{4.8}
\]

The current can also be represented in the energy scale as

\[
J = -\frac{2e}{(2\pi)^3} \int \frac{\hbar^2 k}{m} 4\pi k^2 dE \frac{\hbar^2}{m} \tag{4.9}
\]

For one dimensional flow in small area devices, \( V(x) = \frac{p_x}{m}, \frac{n_4 \pi}{m} \).

The density of states in k-space or \( \frac{dk}{(2\pi)^3} \) as derived in chapter 3 becomes

\[
DOS(E) = \text{const} \times \sqrt{E} \tag{4.10}
\]

To flow, there must be available states just above the Fermi level. For the current, we must add the density of states at the Fermi level \( DOS(E = E_F) \), the Fermi-Dirac state occupation probability \( F(E) \), and can thus describe the current density as

\[
J = -\frac{2e}{\hbar} \int F(E) DOS(E) dE \tag{4.11}
\]

where the intended result is:

\[
\text{Current Density} = qnv \tag{4.12}
\]

\[
\text{Current Density} = \int DOS(E) * \text{Velocity}(E) * F(E) dE. \tag{4.13}
\]
Semi-Classical Electrostatic Screening Part 1

The core concept of Thomas-Fermi screening is that electrons will gather in dense groups around positive ions in a material, effectively hiding the positive charge. To find the charge density in a material that allows this kind of electron movement, it is necessary to find the total potential of the system. This total is the inherent potential caused by the normal electron concentration of the system plus the additional induced potential caused by the increased electron concentration density, as seen in figure 4.1.

![Chemical potential diagram](image)

Figure 4.1: The presence of a positive ion causes electrons to gather together, resulting in a drop in the Fermi level.

The first step in finding the total potential is solving the one electron Schrödinger’s equation [6]. It is also necessary to relate the energy vs. the wave vector of the system in relation to a position $r$, as seen in figure 4.2.

$$E(k) = \frac{\hbar^2 k^2}{2m} - e\phi(r).$$  \hspace{1cm} (4.14)

![E-k diagram](image)

Figure 4.2: E-k diagram in a CeRAM Cell.
Note that some versions of this equation will denote the increased charge density as $U_{\text{eff}}$ instead of $e\phi(r)$. This means that in the uniform electron gas

$$f(E) = f_0(E) = \frac{1}{e^{\frac{E(k) - E_F}{kT}} + 1} = \frac{1}{e^{\frac{(E - E_F)}{kT}} + 1}$$

(4.15)

Polarization leads to a dipole moment $d(\partial n_0 - n_0)$.

$$f_{\text{localized}} = \frac{1}{e^{\frac{(E - E_F) - \phi n_0}{kT}} + 1}$$

(4.16)

Near the atom, there is a space-charge like effect around the ion with two electrostatic potentials. The first, $\phi^{\text{ext}}$ arises from the ion itself. This charge satisfies the Poisson’s equation as seen in [6]

$$-\nabla^2 \phi^{\text{ext}}(r) = 4\pi \rho^{\text{ext}}(r)$$

(4.17)

where $\rho^{\text{ext}}$ is the particle’s charged density. The second charge is $\phi$ which represents the full physical potential of the ion and induced screening charge by the electrons. This charge also satisfies the Poisson equation with

$$\nabla^2 \phi^{\text{total}}(r) = 4\pi \rho^{\text{total}}(r)$$

(4.18)

where $\rho^{\text{total}} = \rho^{\text{ext}} + \rho^{\text{ind}}$. The induced charge $\rho^{\text{ind}}$ can be found with [6]

$$\rho^{\text{total}} = \chi(k)\phi^{\text{total}}(k)$$

(4.19)

The Fourier transform of these Poisson equations leads to

$$k^2 \phi^{\text{ext}}(k) = 4\pi \rho^{\text{ext}}(k)$$

(4.20)

The induced charge $(\phi(k) - \phi^{\text{total}}(k))$ can then be placed into the equation

$$\frac{q^2}{4\pi} (\phi(k) - \phi^{\text{total}}(k)) = \chi(k)\phi(k).$$

(4.21)

Given that charge density $D$ is given with $D = \varepsilon E$ and $\varepsilon_n = \chi - 1$, the following relation will result,
as seen in [6]

\[
\varepsilon(k) = 1 - \frac{4\pi}{q^2} \chi(k) = 1 - \frac{4\pi}{q^2} \rho^{ind} \phi(k).
\]

(4.22)

Thus, the wave vector dependent dielectric constant \( \varepsilon(k) \) can be used in the equation

\[
\phi(k) = \frac{\phi^{ext}(k)}{\varepsilon(k)}
\]

(4.24)

which relates the potential at the atom site to the external and applied potentials. With an applied voltage, the new external potential is

\[
\phi^{ext} = \phi^{ext}_{original} + qV_{applied} = \frac{e^2}{4\pi\varepsilon\varepsilon_0}.
\]

(4.25)

Again, note that some notation systems will label the \( qV_{Applied} \) term as \( U_{eff} \) to show the change in electron density and charge potential.

CeRAM uses this foundation to design materials with desired voltage and current properties to create memory cells. By altering the doping of the material the critical density of electrons can be selected that best fits the requirements of the device design.

Figure 4.3: CeRAM current density vs. voltage diagram.
Semi-Classical Electrostatic Screening Part 2

To find the particle density of electrons moving in a positively charged homogeneous ion sea, it is useful to start with a model that assumes there are no electron-electron interactions (the Sommerfeld model). The distribution of the positive ions will show charge neutrality and will have a constant lattice potential; it also means that the electron density is position-independent

\[ n(r) \Rightarrow \frac{N}{V}. \]  

(4.26)

The system will contain \( N \) electrons in a volume \( V = L^3 \), and these electrons will occupy all states which are less than or equal to the Fermi energy \( \varepsilon_F \)

\[ \varepsilon_0(k) = \frac{\hbar^2 k^2}{2m} \leq \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \]  

(4.27)

The periodic boundary conditions for \( V \) means that the system will have discrete wave numbers

\[ k = \frac{2\pi}{L} (n_x, n_y, n_z); \quad n_{x,y,z} \in \mathbb{Z}. \]  

(4.28)

Since the energy in the system is isotropic (traveling equally in all directions) the electrons will occupy all the states in \( k \) space within a sphere that has a radius of the Fermi wavevector \( k_F \). Since the \( k \)-points in \( k \) space are discrete, each \( k \)-point occupies a grid volume

\[ \Delta k = \left( \frac{2\pi}{L} \right)^3 = \frac{(2\pi)^3}{V}. \]  

(4.29)

With spin degeneracy, each electron space can be occupied by 2 electrons. This means that the total number of electrons in a system is

\[ N = 2 \frac{1}{\Delta k} \left( \frac{4\pi}{3} k_F^3 \right) = 2 \frac{V}{8\pi^3} \frac{4\pi}{3} k_F^3 = \frac{V}{3\pi^2} k_F^3 \]  

(4.30)

This provides a direct relation between the electron number \( N \) and the Fermi wavevector \( k_F \). The wavevector can also be represented as a function of the number of electrons or the electron
density $n_e$

$$k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3} = \left( 3\pi^2 n_e \right)^{1/3}$$  \hspace{1cm} (4.31)

This means the Fermi Energy can be calculated as

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3}$$  \hspace{1cm} (4.32)

With these equations, it is possible to find the unperturbed (position-independent) particle density $n_0$

$$n_0 = \frac{k_F^3}{3\pi^2} = \left( \frac{2me_F}{3\pi^2\hbar^3} \right) = n_0(\varepsilon_F).$$  \hspace{1cm} (4.33)

Now, if an additional charge $q = -e$ is introduced into the system at the origin, the electrons of the system will interact with that charge. In the area near the test charge at $r = 0$, this interaction will generate extra potential energy due to Coulomb repulsion; this energy will be equal to [14]

$$E_{pot}(r) = (-e)\varphi(r)$$  \hspace{1cm} (4.34)

where $\varphi(r)$ is the electrostatic potential of of the test charge. The electrons will avoid the region of $r = 0$, meaning the electron density now becomes position dependent. To find the new electron density function, start with the Schrödinger equation

$$-\frac{\hbar^2}{2m} \Delta \psi_i(r) - e\varphi(r)\psi_i(r) = \varepsilon_i\psi_i(r),$$  \hspace{1cm} (4.35)

and from that the electron density function can be derived as

$$n(r) = \sum_i |\psi_i(r)|^2.$$  \hspace{1cm} (4.36)

The Thomas-Fermi model allows this process to be simplified by allowing the single-particle energies $\varepsilon(k)$ in the presence of the test charge to be written as

$$E(k) \approx \varepsilon(k) - e\varphi(r).$$  \hspace{1cm} (4.37)

This equation is limited as it implies that both a precise position and momentum for the elec-
tron, in violation of Heisenberg’s uncertainty principle. To accept this equation remember that the wave packet of the electron will have an uncertainty of $1/k_F$. This means that the equation requires that $\varphi(r)$ will only change slightly over the a region on the order of $1/k_F$. If transformed into wavenumber-dependent Fourier components, then the Thomas-Fermi approximation will be realistic only in the region of $q \ll k_F$. Applying the Fermi function allows us to find the unperturbed density function in relation to the Fermi energy

$$n_0(\varepsilon_F) = \frac{2}{V} \sum_k (\exp[\beta(\varepsilon(k) - \varepsilon_F)] + 1)^{-1}. \tag{4.38}$$

In order to obtain the perturbed density function, replace the unperturbed energies $\varepsilon(k)$ with the energies $E(k)$

$$n(r) = \frac{2}{V} \sum_k (\exp[\beta(E(k) - e\varphi(r)) - \varepsilon_F]) + 1)^{-1} = \frac{2}{V} \sum_k (\exp[\beta(\varepsilon(k) - e\varphi(r)) - \varepsilon_F]) + 1)^{-1} = n_0(E_F + e\varphi(r)). \tag{4.39}$$

Using the previously calculated unperturbed density function means that the perturbed density function can be rewritten as

$$n(r) = \frac{\left[2m(\varepsilon_F + e\varphi(r))\right]^{3/2}}{3\pi^2h^3} \tag{4.40}$$

Assuming that $\varepsilon_F \gg |e\varphi(r)|$, we can expand $n(r)$ around $n_0$ with a Taylor series and terminate the series after the linear term to simplify the equation to [14]

$$n(r) \approx n_0 + e\varphi(r) \frac{\partial n_0}{\partial \varepsilon_F} = n_0 \left(1 + \frac{3}{2} \frac{e\varphi(r)}{\varepsilon_F}\right) \tag{4.41}$$

Due to the added test charge, a virtual hole forms which allows the positive background charge to show through more strongly than in areas not affected by the test charge. The Coulomb potential of the test charge is thus shielded so the electrons of the system are only affected at distances less than the screening length. In order to calculate the screening length we start with the Poisson equation

$$\Delta \varphi(r) = -\frac{(-e)}{\varepsilon_0} \delta(r) - \frac{(-e)}{\varepsilon_0} [n(r) - n_0] \tag{4.42}$$

The first term on the right side of the equation represents the charge density of the static positive
charge. The second term is a result of the now incomplete compensation of the background positive ion charge in the area of the perturbing charge. Using the previous equation for \( n(r) \), the previous equation can be simplified to

\[
\left( \Delta - \frac{3 n_0 e^2}{2 \varepsilon_0 \varepsilon_F} \right) \varphi(r) = \frac{e}{\varepsilon_0} \delta(r).
\]  

(4.43)

The solution of this equation is best solved using Fourier transformation

\[
\varphi(r) = \frac{V}{(2\pi)^3} \int d^3 q \varphi(q) e^{iq \cdot r},
\]

\[
\delta(r) = \frac{1}{(2\pi)^3} \int d^3 q e^{iq \cdot r}.
\]  

(4.44)

Inserting these into the previous equation yields

\[
\left( -q^2 - \frac{3 n_0 e^2}{2 \varepsilon_0 \varepsilon_F} \right) \varphi(q) = \frac{e}{\varepsilon_0} V.
\]  

(4.45)

If we define

\[
q_{TF} = \sqrt{\frac{3 n_0 e^2}{2 \varepsilon_0 \varepsilon_F}},
\]  

(4.46)

then it is possible to obtain

\[
\varphi(q) = -\frac{e}{\varepsilon_0} V \left( q^2 + q_{TF}^2 \right).
\]  

(4.47)

Using the residual theorem, the reverse transformation is

\[
\varphi(r) = -\frac{e}{2\pi \varepsilon_0 r} \frac{i q_{TF}}{2q_{TF}} e^{-q_{TF} r}.
\]  

(4.48)

When \( r \) is small, this leads to a screened Coulomb potential or Yakawa’s potential of

\[
\varphi(r) = -\frac{e}{4\pi \varepsilon_0 r} \exp(-q_{TF} r).
\]  

(4.49)

As \( r \) approaches infinity, the screened potential drops to zero. If \( r \) is small, this becomes

\[
\varphi(r) = -\frac{e}{4\pi \varepsilon_0 r}.
\]  

(4.50)
Within the screening length

\[ \lambda_{TF} \approx q_{TF}^{-1} = \sqrt{\frac{2\varepsilon_0 \varepsilon_F}{3n_0e^2}}, \tag{4.51} \]

the potential of the test charge is shielded to \(1/e\) of its maximum value. In a metal \(\lambda_{TF}\) has roughly the same magnitude as the spacing of the particles, which means the screening effect is substantial.

A characteristic measure of the strength of this screening effect is given in the dielectric function \(\varepsilon(q,E)\). For this scenario \(E = 0\) and the dielectric function is

\[ \varepsilon^{TF}(q) = 1 + \frac{q^2_{TF}}{q^2}. \tag{4.52} \]

Although \(\varepsilon^{TF}\) is the dielectric function for the electron gas, a total dielectric function that includes the dielectric constant \((\varepsilon_r - \text{the relative dielectric constant of the oxide})\) is

\[ \varepsilon_{\text{Total}} = \varepsilon^{TF} + \varepsilon_r. \tag{4.53} \]

For our purposes only \(\varepsilon^{TF}\) needs to be used (\(\varepsilon_r\) can be set to 0) to show that

1. If \(q \to q_{TF}\) the material is in the insulator phase. Thus, from (4.48)

\[ V_{\text{set}} = \frac{\varepsilon_{TF} U_{\text{eff}}}{e} \approx 2V_{\text{reset}}, \tag{4.54} \]

where \(e\) is the elementary charge (not to be confused with \(q\) which here is a wave vector).

2. If \(q \to q_{\text{Fermi}}\) a metal phase is established.

Since \(\lambda_{TF} = q_{TF}^{-1}\) according to (4.51) and \(q_{TF}\) is proportional to \(n_0\), we can summarize:

1. As \(n_0\) increases \(\lambda_{TF} \to \text{Bohr Radius (a}_B\)). This means that a metal phase dominates.

2. As \(n_0\) decreases \(\lambda_{TF} > a_B\) and a gap appears making the material an insulator.

It is clear that the two states which this system demonstrates leads to two resistances which can in turn be used as a memory.
CHAPTER V

THE CERAM STORAGE CELL DEVICE MODEL

Introduction

The layout for a basic storage cell made with a CeRAM material is shown in 5.1 below. It is a very simple metal-insulator-metal device.

![Figure 5.1: A basic CeRAM storage cell.](image)

What differentiates this device from a semiconductor resistor (MSM) or a passive insulator capacitor is summarized below:

1. The device thickness is below 100 nm, making it a nanoscale two-dimensional device.

2. The insulator material is p-type and the metal makes an ohmic contact without a barrier for holes. (The material is a leaky insulator).

3. The insulator has both wide bands and narrow bands. A narrow band is half-filled and has the Fermi level separating the "highest occupied molecular orbital (HOMO)", from the "lowest unoccupied molecular orbital (LUMO)". This makes the material either a metal - when the HOMO (valence sub-band) and LUMO (conduction sub-band) are overlapping at the Fermi level.

4. Upon injection of electrons from the negative electrode at a critical voltage and current density the excess density completely screens the ions and partially filled (typically 3d states) shell that, due to Hund’s Rule (see below section 5.2), become double occupied. Orbitals with an effective electron-electron repulsive local potential "U", when not screened (i.e. when a lower voltage is applied), electron extraction near the positive electrode (anode) and hole injection
from the anode, expose the local "\( U \)" which is a potential energy much higher than the kinetic energy of the electrons. This phenomenon is called electron localization. The Hamiltonian described by Hubbard and shown in other chapters of this thesis can be shown to have \( U > W \), where \( W \) is the band-width of the narrow band. An energy gap \( E_G = U - W \) appears where the Fermi level is within the band gap. Thus the conductivity \( \sigma = q^2D_nDOS(E = E_F) \) is nearly zero (\( DOS \approx 0 \)) and an insulator phase appears.

5. The device IV curve can be achieved by a triangular or ramp only voltage, which starts at \( V = 0 \) and passes through the voltage needed to turn off \( (V_{\text{reset}}) \) and the voltage that is needed to turn on \( (V_{\text{set}}) \).

6. A differentiator from typical TMO ReRAM, CeRAM starts conducting from \( V = 0+ \). This behavior is called "born-on" which only appears due to carbonyl doping (CO). In section 5.3, the unique properties of CO doping to yield further p-type doping and making "\( U \)" smaller will be shown.

7. Although the complete IV curves and the symmetrical (unipolar, or non-polar) behavior in the first quadrant \( (Q_1) \) with positive voltage and currents and \( (Q_3) \) with negative voltage and current, the most important points points are at the pairs \( (V_C, J_C) \) where \( C = \) critical phase transitions for metal-to-insulator transition (MIT) and insulator-to-metal (IMT) transitions. At these transition points, pulses are applied to yield the final state.

8. As shown in figure 6.1, the storage temperature for \( R_{\text{on}} \) (metal phase) and \( R_{\text{off}} \) (insulator phase) may be over 400 C (limit of test set up) see [15].

9. Operating (switching via a ramp voltage) is shown to go from 4 K to 150 C (see [16]). Recently, the lower temperature has been measured at 1.2 K ([16]). At miliKelvin, if the switching between phases continue, the CeRAM cell will be proven to be a "quantum switch" and the energy of to switch will be small and an almost adiabatic process (i.e. As \( T \to 0 \), no energy loss).

10. Since the screening is localized the microstructure (grains) and grain boundaries have a smaller role in the phase transition (more in the transport). Thus, switching is somewhat
independent of the defects and microstructure (measured down to 100nm x 100nm cell areas) (see [17]).

**Incomplete 3dⁿ Shell TMOs**

To simplify this discussion we will restrict this explanation to NiO. The 1937 seminal paper of de Boer and Verney [9] established the violations of the band theory of Bloch and Wilson in oxides of transition metals. One example is NiO which has an electron structure of \( \{\text{Ar}\}3d^84s^2 \). Notice that 3\( d^8 \) would be a full shell if it would have "10" and not "8" electron states. However, two questions which are the reason for the band theory breakdown are:

1. Since the shell is not full, it means that the Fermi level (separation in energy) between the full band (up to 3\( d^8 \)) and the empty band (3\( d^9 \) and 3\( d^{10} \)) show a valence band and conduction band overlap. (Note: 4\( s^2 \) is a full shell and does not define a Fermi level). Then, why aren’t all these oxides metals?

2. What then is it that make oxides of transition metals (and some rare earths) insulators if this overlap in valence-conduction band shows no energy gap?

The famous discussion between Mott and Peierls [10] took twenty-two years to be demonstrated in the 1959 paper by Mott [11] - a semiclassical description which shows the idea proposed by Peierls that the gap was created by electron-electron repulsion (\( U \)) coming from the narrow bands in these materials.

In fact, as shown below in a step-by-step way, the "3\( d^8 \)" electron structure goes through a split and then a purely electrostatic localized bad gap appears due to Hund’s rule (i.e. the maximization of electron spin) before the electron repulsion blocks "\( U \)" from closing. The end result is that the "electron-electron" interaction (or correlation) make these materials insulators but not caused by the "extended states" of band theory (the Bloch states in a periodic lattice) but localized electron states in each unit cell (no electron wave function overlaps).

Thus, the theoretical electron structure (here for one pair of unit cells), when randomly (or not) repeated to form a solid, show the gap "\( U \)" (and for a full crystal \( E_G = U - W \), where "\( W \)" would be the original (uncapped) band width). Below we show the gap formulation:
A: Ideal non-physical (metal) \( \{ \text{Ar} \} 3d^8 4s^2 \):

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \]

Figure 5.2: 3d8 electron spin configuration.

B: Hund’s rule (to maximize spin) \( \{ \text{Ar} \} (3d^7, 3d^9) 4s^2 \):

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \]
\[ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \]

Figure 5.3: a: 3d7 - 3d9 electron spin configuration.
b: 3d7 3d8 electron spin configuration.

Notice that

\[ \begin{align*}
E_{3d^7} & \quad \text{Valence-like lower Hubbard band (LHB)} \\
& \quad \downarrow U \\
E_{3d^9} & \quad \text{Conduction-like upper Hubbard band (UHB)}
\end{align*} \]

Figure 5.4: 3d7-9 energy gap image.

The electronic structures shown in (B) above are repeated below:
The two initial cells have a structure of $3d^8$ or $Ni^{+2}$. The first cell transitions to the cell on the right and gains a doubly occupied state that is kept together with a repulsive potential energy; this becomes $\{Ar\}(3d^7, 3d^9 - 3d^{10}) 4s^2$ or $Ni^{+1}$. The second initial cell changes to the cell seen at the bottom of 5.5 and becomes $\{Ar\}3d^74s^2$ or $Ni^{+3}$.

It needs to be noted that here "$3d^8$" really means "$3d^7 - 3d^9$", showing that the ideal "$3d^8$" state simply does not exist.

In terms of an equilibrium "disproportionation" reaction, Mott proposed:

$$Ni^{+2}O^{-2} + Ni^{+2}O^{-2} \rightarrow Ni^{+3}O^{-2} + Ni^{+1}O^{-2}.$$  \hspace{1cm} (5.1)

This equation would have an equilibrium constant $K$. It is well known from electro-chemistry that $K$ is

$$K = e^{-\frac{\text{Energy}}{RT}},$$  \hspace{1cm} (5.2)

where the term 'Energy' is $U_{eff}$ when the system is at equilibrium.

In general "energy" means $\Delta G$, the change in Gibbs free energy. However, in a disproportionation reaction $\Delta G = G - G_0$ with $G = U + G_0$, or $\Delta G = U$. This means that only the electrostatic energy ($G_0 = TS^0 + H^0$, where $S^0$ and $H^0$ are the entropy and enthalpy without the electrical free
energy $U$).

Due to the law-of-mass-action

$$K = \frac{[Ni^{+1}][Ni^{+3}]}{[Ni^{+2}]^2} = \text{1 (equilibrium)} \quad (5.3)$$

$$K = e^{-\frac{U}{kT}} \quad (5.4)$$

Clearly this is a quantum effect which induces a band gap purely from Hund’s rule and the doubly occupied state $(3d^9, 3d^{10})$.

As shown in the earlier chapters of this thesis the Hubbard Hamiltonian describes the phase transition from metal-to-insulator or the reverse when

1. The kinetic energy $KE > U$ (metal phase)

2. The potential energy $U > KE$ (insulator phase)

In general, for other transition metal oxides

$$d^n + d^n \rightarrow d^{n+1} + d^{n-1}. \quad (5.5)$$

The "$U$" or as in the Sawatsky model of $\Delta pd$ - in which a hybridization of "3d $- 2p$" of the Ni (3d) and oxygen (2p) creates a "charge transfer gap" for NiO

$$\Delta pd < U. \quad (5.6)$$

The ability to control the conductivity of such materials became the search for a "non-volatile electronic switch" which led to to ReRAMs (with the filaments due to electrostatic soft breakdown of the TMO) and CeRAM (a bulk quantum phenomenon due to carbonyl (CO) doping). Further in this chapter, the device action due to doping will be described.

A key point is that most of these oxides have $3d^{n+1}$ excess, which make them p-type leaky oxides. This is shown in figure 5.6 with the Fermi level close to the LHB.
Carbonyl Doping

Figure 5.3 shows that an oxygen vacancy in a cell disrupts "U" and pins down the Fermi level. Thus the $MO_6$ coordination is no longer in place to cause the disproportionation reaction to appear. It is well know that "CO" takes the place of a missing oxygen atom in "coordinated complexes" such as $MO_6$. In fact, oxygen is just a "ligand" like CO or NH$_3$ in a general description "$ML_6$" of such complexes.

Among basic ligands "CO" (and NO) are known as $\pi$-donors (as well as $\sigma$-donors). This means

$$M \leftarrow CO$$  \hspace{1cm} (5.7)

has a $\sigma$-bond with 2 electrons given to the metal. With $\pi$-back donation the equation becomes

$$M \leftarrow \frac{\sigma}{\pi} CO.$$  \hspace{1cm} (5.8)

The net effect is that the Metal-Carbon bond "fixes" the missing oxygen, or the "coordination sphere" is repaired to $ML_6$. The back donation is a form of the local charge balance to make the metal less electronegative via donation of the charge to lower energy "molecular orbital" states that are empty. This shows that when backdonation occurs, the $M - C \equiv O$ structure becomes $M - C = O$ and the Fermi level which is controlled mostly by the 3$d$ states drops lower and the material becomes more p-type. Thus, conductivity, which is $\sigma_p = q^2 D_p DOS(e = E_F)$, increases as $|E_F - LHB|$ changes (like $E_F - E_V$ in semiconductors). In the next section we will show that this can be combined with the Mott view of screening to create the "switching action" between the metal and insulating states.
CeRAM Device Physics

Now that we have shown:

- The intrinsic property of transition metal oxides to be leaky semiconductors.
- The "technological control" of p-type doping (or the reverse - an n-type oxide could also be a starting point) and that doping lowers the charge gap.

We will see the "device paradigm" upon which CeRAMs were invented. In figures 5.7 and 5.8 we can see that there are four regions of operation. We will describe each region with a figure and the summarized equation that models the device operation below.

![Figure 5.7: CeRAM IV operating quadrants.](image)

![Figure 5.8: CeRAM Resistance vs. root Voltage (R-√V).](image)
Region I is a metal-insulator-metal tunneling diode (MIM - Simon’s model).

Region II occurs when thermionic emission from the cathode overcomes the electron barrier $q\phi_m$ of the MIM diode.

The Mott criteria for the insulator to metal transition is at $V = V_{set} \approx q\Phi_{Bn}$. The turn on point is at $a_B n_{IM}^{1/3} = 0.26$.

Region III is when holes are injected form the anode.

Region IV is the turn off point.
Thus, the CeRAM switch is 'born-on' or there is an ohmic current from $V = 0$ to $V = V_{\text{reset}}$ without first forming a filament as in ReRAMs. Then it turns off (as a FET transistor turns off) with a low gate voltage. Turn-on occurs at roughly $V_{\text{set}} \geq 2V_{\text{reset}}$. Typically $V_{\text{reset}} \approx E_G = U - W$.

In real world operations a square pulse is used. Since the speed of switching is much higher (around 80 femtoseconds for $V_{O_x}$) than the carrier injection (electrons at set and holes at reset) the switching action is nearly adiabatic, making CeRAM an extremely low energy device at hundreds of femtoJoules [16].

Another good property of CeRAM is operation in the region of 1.8 K or below [16]. Since the definition of a quantum phase transition is that it is independent of temperature (only "$U$") there is some evidence of a "quantum switch".

**Model Results**

Figures 5.13 and 5.14 show the theory-to-data comparisons for NiO and YTiO$_3$. Since NiO is a charge-transfer Mott insulator with an NaCl crystal structure (with an octahedral unit cell) and YTiO$_3$ is a Perovskite with an embedded octahedron within a deformed cubic lattice, it is clear that the "CO" doping model can be applied universally in p-type leaky oxides.
Figure 5.13: NiO CeRAM. Graph and data originally produced by Christopher McWilliams [18].
Figure 5.14: YTiO$_3$ CeRAM device characterization, 40nm. Actual data (left) vs. simulation (right).
CHAPTER VI
CONCLUSION AND FUTURE WORK

An Overview of CeRAM

This thesis presented several aspects of a novel phase transition device which is suitable for high speed nonvolatile memory and switches. The central focus was to verify a device model which incorporated the physical, chemical, and technological aspects that cause Mott-like metal-to-insulator and insulator-to-metal phase transitions from an applied bias.

In general, resistive switching from many origins has been tried for over twelve years in the semiconductor industry. This device has its fundamental current-voltage characteristics (I-V) based on a very different mechanism invoking electron-electron strong interactions. For this reason, although the sensing of the state of memory can be seen as a change of resistance from $R_{on}$ (ohmic) to $R_{off}$ (semi-insulating), the underlying physics is shown to be only due to the two-body effect as specified by Mott and demonstrated by Hubbard to be of a quantum mechanical nature.

This thesis proceeded from considering the independent electron model (Ch. III) in which we discussed the zero interaction free electron model and the electron-ion lattice model for metals; or the first type of model with electron-lattice interaction or the zero-order model before the band theory of Bloch and Wilson. Band insulators cannot show metal-insulator phase transitions as these require the local Coulomb interactions to be the single most important potential energy ($U >> E_{Gap}$; where the gap is due purely to lattice periodicity). Thus the paradigm of strong interactions known as the Hubbard Hamiltonian was used. Implementing the Hubbard Hamiltonian, we showed in chapter III that the Mott criteria for metal-to-insulator transitions led to the Slater parameter $r_s = \frac{\text{potential energy}}{\text{kinetic energy}}$. When the Coulombic force ($U = q^2/2\pi\varepsilon_0 r_0$) and the electron kinetic energy ($\hbar^2/nr_0^2$) ratio $r_s$ is used (in the Mott criteria $r_s \approx 0.26/n^{1/3}a_B$) switching between the metal/semi-insulating phase becomes a function of the screening electron density. This being the case, the correlated-electron random access memory (CeRAM) is a device that goes through a technological process (doping) that reduces the $U$ and thus the gap ($E_{Gap} = U - W$, with $W$ being the bandwidth) via the newly discovered double action of $\sigma$-donation and $\pi$-backdonation afforded by carbonyl (CO)
doping of transition metal oxides.

As discussed herein, the combination of band gap reduction (via the "$U$" or "$U_{\text{eff}}$" screening) and the carrier injection action at $V_{\text{set}}$ and $V_{\text{reset}}$ at initial current densities (thus, electron densities as prescribed by Mott) modulated the state transition (switching) and achieved stable measured resistance levels for $R_{\text{on}}$ and $R_{\text{off}}$ up to $400 \, ^\circ\text{C}$ as shown in figure 6.1 below [15].

![Figure 6.1: CeRAM functions at a wide range of temperatures, and can retain the on/off state even when exposed to extreme heat.](image)

The screening mechanism which opens or closes the narrow band due to the "3d" orbitals is the essential "many-body physics" mechanism which was used to show that the electron gas was polarized in different degrees thus inducing the phase transition. This mechanism, although well understood in the metal electron-electron "weak interactions", it was used by Mott in the Thomas Fermi approximation of the static dielectric function ($\varepsilon(k,0)$). A key piece of data needed to establish that this is an "electron-density driver" or Quantum Mott phase transition is shown in figures 6.2 through 6.5 [16]. Notice that a device fails to reset (or turn-off) if the pass gate transistor does not source enough current density and thus electron density to yield the Mott transition. This is central to our drive model as shown in chapters IV and V of this thesis. As figure 6.5 clearly shows, the voltage applied is constant but switching-off is clearly causing screening to be reduced by reverse type carrier injection (p-type in this case) to the carriers injected at the set stage from hot electrons.
\( E = \frac{1}{2}mv^2 \geq q\Phi_B \) coming from the cathode. Thus, as shown in chapter V the model includes:

1. Insulator-to-metal phase transitions at \( V_{set} \),

2. Metal-to-insulator phase transition at \( V_{reset} \),

3. Semi-insulating behavior from tunneling in the Simmons regime, and

4. P-type ohmic behavior which was modulated by carbonyl doping.

In conclusion the essential p-type background doping and the Mott transition regimes at set and reset have created the first fully bulk resistive memory switch. This switch has a greater potential than "filament" based memories that have been the subject of research for "beyond CMOS/FLASH" and artificial synapses in non-Von Neumann computing (AI) [19].

Figure 6.2: 1T1R compliance circuit.
Figure 6.3: Row/column memory cell array.

Figure 6.4: 1T1R DC-IV curves (Constant $V_G$).
Figure 6.5: 1T1R, Constant $V_G$. Reset fails if $I_{DS} < I_{On(Max)}$: proof of the Mott switch.

If the I-V plots of CeRAM devices are normalized, several trends can be seen in the data. In the graph NiO, YTiO$_3$, and HfO$_2$ all show identical reset voltages and similar off current levels. These trends demonstrate that some characteristics of CeRAM devices are universal, and can be applied to multiple materials.

Figure 6.6: Normalized Current-Voltage graphs for multiple CeRAM materials.
<table>
<thead>
<tr>
<th>Data value</th>
<th>NiO</th>
<th>YTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (max)</td>
<td>0.36</td>
<td>1 (normalized)</td>
</tr>
<tr>
<td>V (set)</td>
<td>0.65 V</td>
<td>1.00 V</td>
</tr>
<tr>
<td>V (reset)</td>
<td>1.25 V</td>
<td>1.25 V</td>
</tr>
<tr>
<td>I (off)</td>
<td>0.167</td>
<td>0.167</td>
</tr>
</tbody>
</table>

Table 6.1: Normalized NiO and YTiO$_3$ CeRAM data used for comparison, based off of figure 6.6.

**Future Work**

Since these devices are used in 100-14 nm technology nodes, scaling is the commercially-driven next step. For university materials-driven research a better understanding of materials and the physics of electron-electron interactions in metal-organic materials such as TMO + carbonyl is needed. There is also a need for further brilliant source x-ray spectroscopy. The DARPA research program of [20] covers this area.

For device physics, the seemingly adiabatic switching (no loss of energy) is demonstrated in figure 6.7 from NIST [17] in which, as the temperature approaches 0 K, the device operates normally. Such robustness is useful for space applications, as well as fundamental studies of quantum phase transitions (in fact, no known solid-state device switches in such temperatures).

The notion of quasi-adiabatic switching implies that the dynamic of carrier injection occurs at the time scale much slower than the phase transition (which is the switching with an applied pulse). Future work in pulse response regarding temperature, time, fatigue, etc. is ongoing by device manufacturers. The academic research involved in "pulse modules" and temperature dependence involves sophisticated quantum field theory and especially its thermal and functional integral variety which is beyond the scope of this thesis.

Figure 6.7: Near-adiabatic switching is shown by CeRAM operating at -260 C, 25 C, and 150 C respectively.
REFERENCES


APPENDICES

MATLAB Code

1 % Code created by Chris McWilliams for his 2013 Thesis
2 % Reproduced & modified with permission by Seth Shoemaker
3 % 2019
4
5 hold off
6 clc
7 clear VARIABLES
8 clear fun
9
10 % Physical Constants
11 e=1.60e−19; % Electron charge: Coulombs
12 kB=1.38e−23; % Boltzmann constant: m^2 Kg / s^2 K (K denotes Kelvin)
13 h=6.63e−34; % Planck constant: J−s (not reduced)
14 m=9.109e−31; % Mass of electron: Kg
15
16 %

##############################################################################

17 % Input Parameters
18 n=1000; % Step count
19 s1=50; % Thickness (nm)
20 x1=0:s1/n:s1; % Position (nm)
21 x2=0;
22 K=1; % Permittivity

53
B = 1; % Magnetic field
V = 1.5; % Max voltage
Vapp = 0:(V)/n:V; % Applied Voltage steps
T = 300;
Phim1 = 1.5; % Metal work function Left(eV)
    % default 1.5
Phim2 = 1.5; % Metal work function Right(eV)
phi1 = 1.5; % Barrier height left
phi2 = 1.5; % Barrier height right
A = 100e−12; % Area of device to produce I−V curve

% Barrier equations

dPhi = Phim1 − Phim2; % Metal work function delta (eV)
phi = phi1 + (dPhi − V)* (x1 ./ sl); % Potential Energy (eV)
Vim = −2.88.*s1. /(K*s1. *(s1−x1)); % Image Potential (eV)
Vtot = phi + Vim; % Total Potential

phi p = phi1 − (real sqrt (14.4*(7+Vapp*K*s1)))/(K*s1); % Barrier

% Thermionic current

Ath = (4*pi*m*e*kB^2)/h^3; % Thermionic current
Atun = 4*pi*B*s1*10^-10/h)*real sqrt (2*m); % Tunneling current
% Total current density

J0 = e / (2 * pi * h * (B * s1 * 10^-9)^2); % Total current density

fun = @(x2) phi1 + (dPhi - V) .* (x2 ./ s1); % x2 values are across thickness

F = integral(fun, 0, s1);

phibar = (1 / s1) * F; % average barrier

% Current density due to thermionic emission

phip = phip * e; % convert barrier back to SI units

Jth = Ath * T^2 * exp(-phip / (kB * T)) .* (1 - exp(-(e * Vapp) / (kB * T))); % Current density due to tunneling

phibar = phibar * e * 2.001; % convert to SI units + set average barrier

% height so phibar - eV is never negative.

% Original Tunneling current equation

Jtun = J0 * ((phibar - (e * Vapp)) .* exp(-Atun * realsqrt((phibar - (e * Vapp))) - phibar * exp(-Atun * realsqrt(phibar)));

V_Set = linspace(0, 1.5, 1001);

V_Reset = linspace(0, 1.2, 1001);

V = linspace(0, 1.5, 1001);
Vt=kB*T/e;

J_0=1e-13;

J_Diode=J_0*(exp(V_Set/(2*Vt))-1);

J_ON=J_Diode+abs(exp(-V_Reset/(2*Vt))-1).*realsqrt(V_Reset).*(1-heaviside(V_Set-0.7));

J_tot=Jth+Jtun+J_Diode;

75

76 Figure generation

77 figure(1)

78 subplot(2,2,1);

79 box on

80 plot(Vapp,Jtot,Vapp,J_ON,'--','linewidth',2);

81 xlabel('Applied Bias (V)');

82 ylabel('Current Density (A/cm^2)');

83 legend({'J_{OFF}','J_{ON}'},'location','NorthWest');

84 ylim([0 1])

85 grid minor

86 subplot(2,2,2);

87 box on

88 semilogy(Vapp,Jtot,Vapp,J_ON,'--','linewidth',2);

89 xlabel('Applied Bias (V)');

90 ylabel('Current Density (A/cm^2)');

91 legend({'J_{OFF}','J_{ON}'},'location','SouthEast');

92 axis([0 1.7 10^-12 10^5]);

93 y=[10^-12 10^-11 10^-10 10^-9 10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2];
\begin{verbatim}
10^{-2} 10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5];

set(gca,'ytick',y)
grid minor

I_Tot = A * Jtot;
I_ON = A * J_ON;
I_Diode = A * J_Diode;

subplot(2,2,3);
box on
semilogy(Vapp,I_Tot,'linewidth',2);
xlabel('Applied Bias (V)');
ylabel('Current (A)');
grid minor

ResOn = Vapp./I_ON;
ResOff = Vapp./I_Diode;
SQV = sqrt(Vapp);

subplot(2,2,4);
box on
semilogy(SQV,ResOn,SQV,ResOff,'linewidth',2,'linewidth',2)
xlabel('Root Applied Bias $\sqrt{V}$','Interpreter','latex','FontSize',13);
ylabel('Resistance (Ohm)');
legend({'R_{OFF}','R_{ON}'}, 'location', 'NorthEast');
grid minor
\end{verbatim}
Equation Derivations

MIM Diode Current Simplification

\[ J_{\text{tun}} = J_0 \left\{ \phi \exp(-A_{\text{tun}} \phi^{1/2}) - (\phi + eV) \exp(-A_{\text{tun}} (\phi + eV)^{1/2}) \right\} \]  \hspace{1cm} (A.1)

Assuming intermediate voltages,

\[ \bar{\phi} \approx \phi_0 - \frac{eV}{2} \]  \hspace{1cm} (A.2)

then

\[ J_{\text{tun}} = J_0 \left\{ \left( \phi_0 + \frac{eV}{2} \right) \exp \left[ -A_{\text{tun}} \left( \phi_0 - \frac{eV}{2} \right)^{1/2} \right] - \left( \phi_0 + \frac{eV}{2} \right) \exp \left[ -A_{\text{tun}} \left( \phi_0 + \frac{eV}{2} \right)^{1/2} \right] \right\} \]  \hspace{1cm} (A.3)

\[ J_{\text{tun}} = J_0 \phi_0 \left\{ \left( 1 - \frac{eV}{2\phi_0} \right) \exp \left[ -A_{\text{tun}} \phi_0^{1/2} \left( 1 - \frac{eV}{2\phi_0} \right)^{1/2} \right] - \left( 1 + \frac{eV}{2\phi_0} \right) \exp \left[ -A_{\text{tun}} \phi_0^{1/2} \left( 1 + \frac{eV}{2\phi_0} \right)^{1/2} \right] \right\} \]  \hspace{1cm} (A.4)

Assume \( eV/2 >> 1 \).

\[ J_{\text{tun}} = J_0 \phi_0 \left\{ - \left( \frac{eV}{2\phi_0} \right) \exp \left[ A_{\text{tun}} \phi_0^{1/2} \left( \frac{eV}{2\phi_0} \right)^{1/2} \right] - \left( \frac{eV}{2\phi_0} \right) \exp \left[ -A_{\text{tun}} \phi_0^{1/2} \left( \frac{eV}{2\phi_0} \right)^{1/2} \right] \right\} \]  \hspace{1cm} (A.5)

\[ = -J_0 \frac{eV}{2} \left\{ \exp \left[ A_{\text{tun}} \phi_0^{1/2} \left( \frac{eV}{2\phi_0} \right)^{1/2} \right] + \exp \left[ -A_{\text{tun}} \phi_0^{1/2} \left( \frac{eV}{2\phi_0} \right)^{1/2} \right] \right\} \]  \hspace{1cm} (A.6)

\[ = -J_0 \frac{eV}{2} \left\{ \exp \left[ A_{\text{tun}} \left( \frac{eV}{2} \right)^{1/2} \right] + \exp \left[ -A_{\text{tun}} \left( \frac{eV}{2} \right)^{1/2} \right] \right\} \]  \hspace{1cm} (A.7)

This reduces to:

\[ J_{\text{tun}} = -J_0 \frac{eV}{2} \exp \left[ A_{\text{tun}} \left( \frac{eV}{2} \right)^{1/2} \right] \]  \hspace{1cm} (A.8)

Tunneling Current

\[ J = \frac{2q}{\hbar} \int \left( \frac{\Gamma_1 \Gamma_2}{\Gamma_1 + \Gamma_2} \right) (f(E) - f(E - eV)) \rho_{\sigma d} dE. \]  \hspace{1cm} (A.9)
Given that the system has similar electrodes, the coupling constants \( \Gamma_0 = \Gamma_1 = \Gamma_2 \). Therefore,

\[
\frac{\Gamma_1 \Gamma_2}{\Gamma_1 + \Gamma_2} = \frac{\Gamma_0^2}{2\Gamma_0} = \frac{\Gamma_0}{2}.
\] (A.10)

This reduces the current density equation to:

\[
J = \frac{2q}{\hbar} \int \frac{\Gamma_0}{2} \left( f(E) - f(E - eV) \right) \rho_\sigma dE.
\] (A.11)

\[
J = \frac{q}{\hbar} \int \Gamma_0 \frac{\Delta f}{N} \sum_k \delta(E - \epsilon(k) - \Sigma) dE
\] (A.12)

\[
= \frac{q\Gamma_0}{hN} \int \Delta f \sum_k \delta(E - \epsilon(k) - \Sigma) dE
\] (A.13)

\[
= \frac{q\Gamma_0}{hN} \int (f_L(E) - f_R(E - eV)) \sum_k \delta(E - \epsilon(k) - \mu - \Sigma) dE
\] (A.14)

\[
= \frac{q\Gamma_0}{hN} \sum_k J_0[f_L(E - \epsilon(k) - \mu - \Sigma) - f_R(E - \epsilon(k) - \mu - \Sigma - qV)]
\] (A.15)

\[
= \sum_k J_0 \left[ \frac{1}{\exp(E - \epsilon(k) - \mu - \Sigma) + 1} - \frac{1}{\exp(E - \epsilon(k) - \mu - \Sigma - qV) + 1} \right]
\] (A.16)

\[
= \sum_k J_0 \left[ \begin{array}{c} e^{-\beta \exp(E - \epsilon(k) - \mu - \Sigma)} - e^{-\beta \exp(E - \epsilon(k) - \mu - \Sigma - qV)} \end{array} \right]
\] (A.17)

\[
= \sum_k J_0 \left( e^{-(E - \epsilon(k))/kT} \right) \left( 1 - e^{qV/kT} \right)
\] (A.18)

**Low Resistance State Current Equation Derivation**

\[
\rho_0(E) = \frac{1}{N} \sum_k \delta(E - (E(k) - \mu))
\] (A.19)

Since the system is at the Fermi level, let \( \mu = 0 \).

\[
\rho_0(E) = \frac{1}{N} \sum_k \delta(E - E(k)) \frac{\hbar^2 k^2}{2m + V(x)}
\] (A.20)
Changing to integration based on $\sum_k \rightarrow \int dk^3$.

$$\rho_0(E) = \frac{1}{N} \sum_k (E - E(k))$$ \hspace{1cm} (A.21)

$$= \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \int \delta \left( E - \frac{\hbar^2 k^2}{2m} \right) dk^3$$ \hspace{1cm} (A.22)

$$= \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \int \int \int \delta \left( E - \frac{\hbar^2 k^2}{2m} \right) (k \cos(\theta)) (k \sin(\theta)) dk$$ \hspace{1cm} (A.23)

$$= \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \int_0^\infty K^2 \delta(E - \frac{\hbar^2 k^2}{2m}) dk$$ \hspace{1cm} (A.24)

The trick is to go from

$$\delta(x^2 - \alpha^2) \to \frac{1}{2|\alpha|} (\delta(x-\alpha) + \delta(x+\alpha))$$ \hspace{1cm} (A.25)

$$\delta(E - \frac{\hbar^2 k^2}{2m}) = \delta \left( \frac{\hbar^2}{2m} \left( \frac{2mE}{\hbar^2} - k^2 \right) \right)$$ \hspace{1cm} (A.26)

If we use

$$\delta(\alpha x) = \frac{1}{|\alpha|} \delta(x)$$ \hspace{1cm} (A.27)

then

$$\left( \frac{2m}{\hbar^2} \right) \delta(x^2 - k^2) = \left( \frac{2m}{\hbar^2} \right) \frac{1}{2|k|} \delta(x-k) + \delta(x+k)$$ \hspace{1cm} (A.28)

so,

$$\rho_0(E) = \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \int_0^\infty k^2 \delta \left( E - \frac{\hbar^2 k^2}{2m} \right) dk$$ \hspace{1cm} (A.29)

$$= \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \left( \frac{2m}{\hbar^2} \right) \int_0^\infty k \left\{ \delta \left( \sqrt{\frac{2mE}{\hbar^2}} - k \right) + \delta \left( \sqrt{\frac{2mE}{\hbar^2}} + k \right) \right\} dk$$ \hspace{1cm} (A.30)

$$= \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \left( \frac{2m}{\hbar^2} \right) \int_0^\infty k \delta \left( \sqrt{\frac{2mE}{\hbar^2}} - k \right) dk$$ \hspace{1cm} (A.31)

With $\delta(x) = \delta(-x)$

$$\rho_0(E) = \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \left( \frac{2m}{\hbar^2} \right) \frac{1}{2} \int_0^\infty k \delta \left( k - \sqrt{\frac{2mE}{\hbar^2}} \right) dk$$ \hspace{1cm} (A.32)

$$\rho_0(E) = \frac{1}{N} \left( \frac{V}{(2\pi)^3} \right) \left( \frac{2m}{\hbar^2} \right) \sqrt{\frac{2mE}{\hbar^2}}$$ \hspace{1cm} (A.33)
This simplifies to $\rho_0 = C \sqrt{E}$ as expected.

For the current equation up to the phase transition in the on state:

$$\sigma_p = q^2 D_p(\rho_0)(E) \quad (A.34)$$

$$J_{\phi_p} = \frac{2q}{\hbar} \int (((1 - f_L(E)) - (1 - f_R(E - qV)))\rho_0(E) dE \quad (A.35)$$

$$= -\frac{2q}{\hbar} \int (f_L(E) - f_R(E - qV))\rho_0(E) dE \quad (A.36)$$

$$= -\frac{2q}{\hbar} (f_L(E) - f_R(E - qV))\rho_0(E) \Delta E \quad (A.37)$$

$$= -C (f_L(E) - f_R(E - qV)) \sqrt{E_v - E} \quad (A.38)$$

$$= -Ce^{-\beta(E-E_F)} \left(1 - e^{\beta qV}\right) \left[\sqrt{E_v - E(k) + qV}\right] \quad (A.39)$$
### Experimental Data - NiO Characterization

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