A STUDY OF CHARGE TRANSPORT PHENOMENA AND NANOSCALE
INVESTIGATION OF THE MODIFIED CdS SURFACE

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A STUDY OF CHARGE TRANSPORT PHENOMENA AND NANOSCALE
INVESTIGATION OF THE MODIFIED CdS SURFACE

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The adsorption of 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1\textsuperscript{3,7}]decane (7ETTD), polyaniline (PANI), triethoxysilane (TES), and poly(methyl methacrylate) (PMMA) on ultrathin sputtered amorphous CdS films has been investigated using inelastic electron tunneling spectroscopy (IETS), in conjunction with multiple reflection adsorption IR spectroscopy. Conductance–voltage data are recorded for tunnel junctions of the type Al/CdS/7ETTD/Pb over a temperature range of 4K to room temperature and they indicate that the presence of the adsorbed 7ETTD layer on the CdS dramatically modifies the conductance – voltage behavior of the junctions. These measurements show that different conduction mechanisms, including tunneling and possibly hopping, are responsible for charge transfer through the junctions depending on current, temperature, and voltage. WKB fits to the data are used to determine tunnel barrier parameters (height and width) for Al/CdS/Pb junctions with and without adsorbed 7ETTD layers on the CdS. Analysis of the fits shows that tunneling occurs at low bias (less than ~0.2 V) but, at higher bias voltages, modification of the barrier parameters alone is insufficient to account for the observed conductance changes. A frontier orbital model is invoked which does offer a plausible explanation for these conductance changes. The model assumes bias-dependent coupling between HOMO and LUMO states of the adsorbed 7ETTD and surface states on the CdS.
present work suggests that, because of the marked effect on the conductance of CdS ultra-thin films, 7ETTD and other similar compounds may be candidates for use in molecular electronic device fabrication.

It was found that PANI and TES do not adsorb strongly on amorphous CdS but can be used to modify conductance-voltage behavior. On the other hand, PMMA adsorbs strongly and shows promise as a material for use as a host matrix, in photovoltaic applications.

Preliminary work is presented in which CdS nanoparticles size is estimated using surface enhanced Raman spectroscopy and Atomic Force Microscopy, and it has been determined that IETS and conductance-voltage measurement could be extended for the investigation of CdS nanoparticles electronic properties. Further investigations into the surface properties of CdS are presented. Specifically, a robust technique, based on vertical, “z-lift”, manipulation of a negatively biased oscillating atomic force microscope tip, is extended to CdS and used to create raised columnar nanostructures with high aspect ratios (up to 40 nm high/150 nm wide) on amorphous CdS thin films. The nanostructures' height 8–40 nm can be controlled and correlates with CdS film thickness. An in-house modified electric force microscope is used to record the associated surface charge distribution in the proximity of the nanostructures which is found to be opposite to that of the tip.
DEDICATION

To my family.
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CHAPTER I

INTRODUCTION

Nanotechnology has emerged over the last decade as a highly promising area of interdisciplinary research, particularly in the areas of physics, chemistry and engineering. While developments in computers, industry, and science in general were rapid and widespread in the twentieth century, nanoscience has the potential to open the door for us in the 21st century. Understanding the underlying chemical and physical processes on a nanoscale allows us to tap into a wide range of technological applications. Despite the fact that this topic has been a focus of much of the work during the past decade, and that people have been using nanotechnology in an empirical sense since ancient times, a good example being the Lycurgus Cup, much remains to be understood. A better comprehension of this part of science could generate significant growth of new technology.

One of these areas is the exploration of new, renewable sources of energy. The beginning of 21st century is associated with novel scientific ideas, and exciting development of technology and engineering, but the lightning growth of industry is inextricably linked to depletion of the earth’s energy resources and the need for additional sources of energy for manufacturing as well as basic energy needs. While the finite available energy resources of the earth are being
consumed, many renewable sources such as wind, geothermal, nuclear, and solar are being explored. Of these, solar is particularly interesting as it will be present and available for the duration of our planet’s lifetime.

The development of solar panels began in the early 1950s, and historically can be divided into three generations. The first generation is associated with crystalline materials and has its scientific roots in solid state physics. The needs were very simple and without wide application. It was developed as a constant source of energy for space applications or remote hard to reach locations, where the delivery of fuels or others sources of energy is a problem. The efficiency of the best crystalline solar cells is currently 27% . The second generation of solar energy sources is based on amorphous materials and has advantages in cost, ease of production, and durability. The efficiency of amorphous devices is steadily increasing and still has potential for further improvements. The latest generation of solar cells is targeting efficiencies up to 60 %. And scientists have in their arsenal a number of technological innovations to work with. One of which is using nanotechnology to create multijunctional cells or multiple absorption bands to extract maximum energy from the available solar spectrum.

CdS has been widely used in photovoltaic applications for several decades because it has a direct bandgap of 2.5 eV, which is in of the peak output region of the solar spectrum. Along with CdTe, it can be used for heterojunction applications in tandem junctions. It has also been proven to be a valuable and promising material for nanotechnology. CdS nanoparticles have a tunable bandgap with a relatively wide range from 2.5 to 4 eV. An understanding of
charge transfer mechanism in CdS and CdTe thin film and nanoparticles is crucial, not only from a fundamental scientific perspective, but also in designing more efficient photovoltaic devices. An investigation of charge transport in CdS films and nanoparticles form the basis of a major part of this dissertation. Surface functionalization of these materials is also important, where the surface area of active photovoltaic composite layers can be increased. Functionalization of CdS films, investigated by employing a new modified scanning probe technique, is described.
2.1 Interfaces and their modification

The interfaces between semiconductors or semiconductors and other materials are very important and determine the electronic properties of almost all semiconductor devices. A number of factors influence these properties, including:

- the difference between the electron affinities of involved materials
- the difference in the structure of the materials
- interface defects
- interactions between materials, including induction effects

Modification of the interfaces can change the properties of the material and create new possibilities for developing semiconductor devices. Therefore, it is crucial to understand the mechanisms of such modifications. The general acid–base concept is not capable of explaining band bending, an important phenomenon in the study of adsorption on semiconductors and change in electrons affinities of semiconductor interfaces. A classical chemical explanation of donating or accepting electrons does not include quantum phenomena.

Passivation is one of the methods of chemical modification of the surface by
termination of bonds to assure chemical stability. A more detailed consideration of the interaction is needed to elucidate the effects of passivation of the surface. Cohen et al focused on applying a Frontier Orbital Model to explain modification of semiconductor surfaces with experimental evidence that strongly supports this approach [1]. The authors showed a series of experiments that use several types of aromatic substituents on dicarboxylic acids derivatives to dope the interface of n- and p- type GaAs. Another paper [2] by the same group uses the same approach to relate molecular parameters to band bending and electron affinity changes. Both papers introduce the frontier orbital model as a method of explaining changes in the surface charge and band bending.

2.2 Semiconductor surface states and band bending

In general, atoms at the surface have different bonding character to those in the bulk. The reason is simple: at the interface there are no neighbors to repeat the structure of the bulk material. The change in the bonding creates deformation of the surface structure and ionization of the surface. Such surface reconstruction minimizes the surface energy and establishes so-called electronic surface states, which are different from the bulk. In other words, surface states and vacancy levels are caused by dangling bonds. Just like regular energy levels, dangling bonds can have bonding and antibonding character. Those are the states that will interact with foreign atoms at the interface.

The surface potential is different from the bulk potential of electrons trapped in the surface states. The Fermi level defines whether the available states will be
empty or filled. At the interface of two or more materials, under zero bias, the Fermi level is constant throughout the electron path in a semiconductor. Therefore, the energy of surface states with respect to the Fermi level defines the charge trapped on the surface and the degree of band bending. A p-type semiconductor has bands, which are bent “downwards” as one approach the surface, while for n-type semiconductors they are bent “upwards”, since the charge that accumulates on a surface is negative (Figure 1).

![Diagram](image)

**Figure 1.** Schematic energy level diagram illustrating band bending in a) an n-type semiconductor, b) a p-type semiconductor. Surface states are shown as dashed lines.
2.3 Frontier Orbital Model

The Frontier orbital model is a quantum mechanical approach to explain the interaction of two systems. Consider two interacting orbitals with unperturbed wave-functions $\psi^0_1$ and $\psi^0_2$. By invoking first order perturbation theory, new orbital will have a wave-function

$$\psi_1 = \psi^0_1 + \frac{\langle \psi^0_2 | H | \psi^0_1 \rangle}{E^0_1 - E^0_2} \psi^0_1,$$

where $H$ is the Hamiltonian operator and $E^0_1$, $E^0_2$ are the energy levels of $\psi^0_1$ and $\psi^0_2$ respectively.

The matrix element $\langle \psi^0_2 | H | \psi^0_1 \rangle$ determines the symmetry rules for the interaction. Since the Hamiltonian $H$ is totally symmetric, only orbitals with the same symmetry will interact. The dominator in (1) will determine the strength of the interaction, which is the coupling between two states. The closer the energy of the interacting orbitals, the stronger the interaction will occur. In any reaction the highest occupied molecular orbital (HOMO) containing electrons of one molecule will interact with an empty lowest unoccupied orbital (LUMO) of another molecule to form new bonding and antibonding orbitals. Such kinds of interactions will lower the energy of the occupied orbital and will determine the energy of the unoccupied orbital, while lowering the energy of the system overall.
2.4 Applications of the Frontier Orbital Model

The frontier orbital model satisfies the Usanovich acid-base definition, which states that any reaction producing a salt should be considered as an acid-base reaction. The Lewis definition of acids and bases can also be reformulated in terms of frontier orbitals: “A base has an electron pair in a HOMO of suitable symmetry to interact with the LUMO of the acid (although lone pair orbitals with the wrong geometry may need to be ignored)” [3].

The degree of band bending at semiconductor interfaces depends mostly on the surface charge that accumulates due to surface states. It has been shown that surface states can be modified by the adsorption of dicarboxylic acid derivatives (DCA) on semiconductor surfaces such as CdTe [2]. The binding group is the same for all DCAs and has no effect upon the change of band bending and has been chosen as a passivation agent based on previous studies of adsorption [4] and it is known that carboxylic acid is a good adsorption group. The LUMO level of such molecules can be changed if one makes changes in the aromatic substituents (Figure 2). The dipole moment of the molecule will also be different.

![Figure 2. Schematic presentation of dicarboxylic acid derivatives: a) dicyano- (DCDC), b) dihydrogen- (DHDC) c) dimethoxy- (DMDC)](image)

Figure 2. Schematic presentation of dicarboxylic acid derivatives: a) dicyano- (DCDC), b) dihydrogen- (DHDC) c) dimethoxy- (DMDC)
Cohen et al [1] take the experimental approach of investigating different types of semiconductors: p- and n-type GaAs. High defect levels tend to pin the Fermi level at the surface, at a position that is essentially independent of the adsorbate. The position of surface states and band bending at interfaces have been explored by surface photovoltage spectroscopy (SPS). SPS was introduced in 1972 by Harry C. Gatos and Jacek Lagowski [5] and remains one of the most efficient and simple ways to characterize surface states.

Upon illumination of a semiconductor surface with photons, whose energy is less than the bandgap, excitation of the electrons that occupy surface states can occur. The transition of excited electrons to the conduction band will increase the contact potential difference (CPD). By changing the energy of incident photons, and observing the CPD, one can determine the energy of surface states and the changes in band bending. When increasing the energy of photons to the level of the energy difference between the surface state and the conduction band, an electron that occupies this state can be excited to the conduction band and become a charge carrier. That will increase the CPD. It is relatively straightforward to determine the band bending once the charge distribution on the surface is known, using Poisson's equation:

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon},$$  \hspace{1cm} (2)

where $\varphi$ is the surface potential, $\rho$ is the charge distribution and $\varepsilon$ is the dielectric constant of the semiconductor. Equation (2) can be solved for $\varphi$, which is responsible for the band bending.
Figure 3 schematically represents the frontier orbital approach for the explanation of modifying the surface of n-type semiconductor. The interaction of the LUMO of the adsorbent and HOMO of the semiconductor (in this case surface states occupied by electrons) forms a LUMO high above the Fermi level and a new HOMO down in the valence band. Lowering the surface states forces electrons to be delocalized in the VB, which reduces the net charge on the interface.

(a) LUMO LUMO of the DC molecule
(b) New HOMO and LUMO states of the semiconductor

Figure 3. MO Diagram of a HOMO-LUMO interaction (a) between two molecules (b) between the semiconductor surface and adsorbed molecule.
Electrons are no longer trapped at the surface as they were with the unmodified semiconductor surface. Reducing the charge on the surface automatically reduces the band bending. In case of a p-type semiconductor the majority carriers are holes, positively charged virtual particles, and surface states are now located above the Fermi level near the conduction band. Now surface states play the role of HOMO levels in HOMO-LUMO interactions, since they are empty because of their location above the Fermi level. When the surface interacts with adsorbed molecules, those states are pushed up to the conductance band, which decreases the positive charge on the surface. Therefore, the band bending also decreases. A simple acid-base treatment, which invokes transferring electrons, fails to explain this effect, since the change of the surface charge doesn’t depend on whether the sample was n- or p- type. An acid removes a pair of electrons, leaving a base positively charged.

The strength of the coupling between molecular orbitals depends on their mutual location. The further the levels are away from each other the smaller the interaction will be.

2.5 Organic solar cells

During the last decade, organic solar cells and other electronic devices have become a reality. Organic semiconductors are essentially molecular solids, and their properties, such as a charge density, are highly localized within the molecules. Despite the fact that power conversion efficiencies for purely organic photovoltaic devices are still around 5% or less, they have some undisputable
advantages: (1) flexibility, (2) continually tunable bandgap, (3) low cost on an industrial scale, and (4) versatility of fabrication methods. Nevertheless, despite these advantages, they still have limited lifetime and durability. Investigation of the losses in organic materials is a rapidly growing topic of research [6]. Other problems that need to be overcome are matching the devices spectral operating range with that of the solar spectrum without reducing the open circuit voltage [7], and exciton loss limitations on the thickness of absorption material [8]. Charge mobility is another disadvantage of organic materials over inorganic. It is several orders of magnitude lower than in crystalline inorganic materials and significantly lower than in amorphous materials.

2.6 Hybrid heterostructures

These devices combine useful properties of organic and inorganic materials. An innovative approach receiving current attention in this area is the use of nanomaterials. Inorganic nanoparticles are a relatively new class of materials whose properties can be altered by processes arising from quantum confinement. There are many advantages to using hybrid devices, such as optimized tandem solar cells. For example, their bandgap energy can be modulated, they have a large absorption cross-sections, and a large separation in discrete energy levels.
2.7 Conduction mechanisms

The importance of understanding the mechanisms and laws regarding electron transport in semiconductor materials and organic molecules involving metallic contacts cannot be overestimated. Semiconductor-metal interfaces have been a hot topic in the scientific literature since the mid 20th century [9]. The study of organic materials has been very popular in the last decade [10, 11, 12].

Electronic transport mechanisms have been widely and intensively investigated and have been divided into six major categories for thin film metal insulator metal (MIM) junctions. These mechanisms show different behavior depending on the structure of the insulator molecules, distance between metal electrodes and temperature (Table 1) [13] and are outlined below. They will be dealt with more detail in the Results and Discussion section.

2.7.1 Tunneling

Tunneling is a purely quantum mechanical phenomenon and relies on the fact that electron wavefunctions are not discontinuous at tunnel barriers but, rather exponentially decay with the thickness of the barrier. If the barriers are sufficiently low and thin, there is a small probability that the wavefunction will penetrate the barrier and emerge on the other side (Figure 4). There is a small temperature dependence of the tunneling current and the current is proportional to the applied voltage. Diffusive tunneling is a process similar to coherent tunneling with the exception that the tunneling now occurs
Table 1. Conduction mechanisms in MIM junctions

<table>
<thead>
<tr>
<th>Name of the mechanism</th>
<th>temperature dependence (T)</th>
<th>voltage dependence (V)</th>
<th>thickness dependence (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical tunneling</td>
<td>No dependence</td>
<td>low voltages $\sim V$</td>
<td>$\exp(-\beta d)$</td>
</tr>
<tr>
<td>Diffusive tunneling</td>
<td>No dependence</td>
<td>low voltages $\sim V$</td>
<td>$\exp(-\beta d)$</td>
</tr>
<tr>
<td>Ohmic (&quot;hopping&quot;)</td>
<td>$\exp(-\alpha / T)$</td>
<td>$\exp(\gamma V^{1/2})$</td>
<td>$\exp(-\beta' d^{1/2})$</td>
</tr>
<tr>
<td>Frenkel-Poole emission</td>
<td>$\exp(-\alpha / T)$</td>
<td>$\exp(\gamma V^{1/2})$</td>
<td>$\exp(-\beta' d^{1/2})$</td>
</tr>
<tr>
<td>Thermionic emission</td>
<td>$\exp(-\alpha / T)$</td>
<td>$\exp(\gamma V^{1/2})$</td>
<td>$\exp(-\beta' d^{1/2})$</td>
</tr>
<tr>
<td>Fowler-Nordheim emission</td>
<td>No dependence</td>
<td>$V^{2} \exp(-\gamma / V)$</td>
<td>$\exp(-\beta d)$</td>
</tr>
</tbody>
</table>

$\alpha$, $\beta$, $\beta'$, and $\gamma$ are constants independent of temperature, distance, and voltage respectively.
through multiple sites, which can be represented as series of potential wells. Fowler-Nordheim tunneling is a distinctive mechanism, which is more strongly reliant on voltage than direct tunneling. Charge carriers traverse thinner regions of the barrier in the Fowler-Nordheim regime. There is no temperature dependence for this mechanism.

![Figure 4](image)

**Figure 4.** The initial and the final state wave function are exponentially attenuated inside the tunnel barrier, while they are sinusoidally varying outside.

### 2.7.2 Thermionic emission

Thermionic emission is the ejection of electrons or ions from the surface of a material when the thermal energy of the ions, kT, exceeds the potential barrier height or in the case of a metal, the work function [14]. Electrons in a metal or semiconductor are distributed according to the product of density of states and Fermi-distribution function, which is temperature dependent. Therefore, at sufficiently high temperatures, electrons with enough energy may travel over the barrier classically. Thermionic emission is easily recognizable due to its high temperature and voltage dependence.
2.7.3 Poole-Frenkel emission

Poole-Frenkel emission is the process of field enhanced thermal excitation of electrons from defect centers within the dielectric or semiconductor barrier. The process is very similar to the Schottky effect where trap states are the supply of electrons and therefore the barrier height is the energy of the trap and the barrier reduction is larger than in Schottky emission due to immobility of the charge [15]. Poole-Frenkel emission is the basic conduction mechanism in insulators. After thermal excitation, the electrons will move through crystal before relaxing into another localized state.

2.8 Inelastic Electron Tunneling Spectroscopy

Inelastic Electron Tunneling Spectroscopy (IETS) was discovered in 1966 by Jacklevic and Lambe [16]. These workers were able to relate subtle features in the current-voltage dependence of MIM tunnel junctions to vibrational spectra of materials comprising the insulating tunnel barrier. At first sight, IETS might appear to be less capable than other widely used techniques such as Infrared and Raman. For bulk samples, IR and Raman spectroscopy would be the best choice. Indeed, for thick adsorbed layers on large surface areas, Infrared and Raman are also appropriate. But for thin layers and high energy loss surfaces IETS is intrinsically more sensitive than other forms of vibrational spectroscopy.

Tunneling processes in quantum mechanics, can be understood in terms of the solutions of the Schrödinger equation. The rate at which tunneling occurs is determined by the exponential decay of the wavefunction in the classically
forbidden region. For many purposes this rate can be estimated using the WKB approximation [17].

Consider the potential barrier associated with the insulating layer between metal 1 and 3 of the form shown in Figure 4. Utilizing the WKB approximation, solutions of Schrödinger equation are of the form:

\[ D = \exp(-2K) \]  \hspace{1cm} (1)

where \[ K = \int_{x_2(E_x)}^{x_1(E_x)} \kappa(x, E_x) dx \] \hspace{1cm} (2)

and \[ \kappa(x, E_x) = \left( \frac{2m[V(x) - E_x]}{\hbar^2} \right)^{1/2} \] \hspace{1cm} (3)

In equations (1)-(3) \( E_x \) is the kinetic energy; \( x_1, x_2 \) are the classical turning points; \( V(x) \) is the potential energy; and \( D \) is properly regarded as the transmission factor. The probability current is defined as

\[ j = \frac{i\hbar}{2m} \left( \psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right) \] \hspace{1cm} (4)

The WKB approximation implies that the potential in the metal-insulator-metal (MIM) system varies slowly compared to electron wavelength. The net current density is given by

\[ J = J_{12} - J_{21} \] \hspace{1cm} (5)

\[ J_{12} = \frac{2e}{(2\pi)^3} \iiint d^2k_x dk_x \left( \frac{1}{\hbar} \frac{\partial E}{\partial k_x} \right) D_f(E) \left[ 1 - f(E + eV) \right] \] \hspace{1cm} (6)

\[ J_{21} = \frac{2e}{(2\pi)^3} \iiint d^2k_x dk_x \left( \frac{1}{\hbar} \frac{\partial E}{\partial k_x} \right) D_f(E + eV) \left[ 1 - f(E) \right] \] \hspace{1cm} (7)
\[ J = \frac{2e}{(2\pi)^3} \int_{0}^{\pi} dE_x \left[ f(E) - f(E + eV) \right] \int d^2 k_x D(E_x, V) \]  

(8)

\( J_{12} \) can be obtained by integrating over all available \( k \) states in metal 1, multiplying each \( k \) by the corresponding group velocity \( v_x \) and the transmission factor \( D(E_x) \) and by the Fermi function, to make sure that the initial state is occupied and the state 2 is empty. The factor 2 in these formulas represents the spin degeneracy, \((2\pi)^3\) reflects the number of states per unit volume in \( k \) space. The WKB approximation is usually invoked to determine the following expression for tunnel current density:

\[ j = \frac{2e}{\hbar} \int_{-\infty}^{\infty} \exp \left( -\frac{2}{\hbar} \int_{0}^{d} \left[ 2m[\varphi(x, V) - E_x] \right]^{1/2} dx \right) \times \left[ f(E) - f(E - eV) \right] dE_x \]  

(9)

where \( \hbar \) is Planck’s constant, \( \hbar = h/2\pi \), \( e \) is the electronic charge, \( x \) is the distance into the barrier, \( d \) is the total thickness of the barrier, \( E \) is the total energy of the tunneling electrons, \( E_x \) is the \( x \) component of the energy, and \( \varphi(x, V) \) describes the barrier potential.
2.9 Principles of IETS

Figure 5(a) is a schematic diagram of a MIM structure, with a bias $V$ applied across the junction [17], [18]. Two basic mechanisms are involved in the procedure of recovering the vibrational spectrum of the insulating layer of MIM sandwiches. The first mechanism is an inelastic threshold spectroscopy.

Figure 5 (b) and (c) represent an energy band diagram of the tunnel junction with bias $V=0$, and $V > 0$ respectively applied across the junction. If the potential barrier is thin enough there is a small probability that incident electrons will tunnel through the classically forbidden region. Most of the electrons will tunnel without losing energy; this is an elastic process. However, approximately 1% will tunnel inelastically giving up their energy $\hbar \omega_p$ to excite vibrational modes in the molecules forming the barrier, where $\hbar \omega_p$ is the energy associated with a particular vibrational mode of the molecule. The required bias voltage has to satisfy the condition $eV \geq \hbar \omega_p$. This inelastic process can be considered as an additional channel for current flow across the barrier. [19]. Therefore, the total current across the junction will be increased at bias voltage $V = \hbar \omega_p$ (see Figure 6). This increase in the current will result in a step function (ideally at temperature 0 K) on a $dI/dV$ versus bias voltage $V$ plot Figure 6(b) and a peak on a $d^2I/dV^2$ versus bias voltage plot. Therefore, one can construct the vibrational spectrum of the molecules in the barrier by plotting second derivative of the current with respect to voltage versus bias voltage, where the peaks will correspond to vibrational modes.
Figure 5. Schematic diagram of a MIM tunnel junction structure. Junction under conditions of applied dc bias (a) with the corresponding energy band diagram of the structure (b) for zero bias (c) for a positive potential applied to metal 2.
Figure 6. Schematic I-V curve showing how the total current is a sum of contribution due to elastic and inelastic currents (a) with the slope change in plot results in a step function in the first derivative plot (b) and a peak in the second derivative plot at 0 K (c) (the dashed line represents thermal smearing of the curves at non zero temperatures).
In order to recover second derivatives of the current experimentally, one can use phase-sensitive modulation techniques. Both current and voltage can be modulated to find position of the peaks since the position of the peaks in $d^2I/dV^2$ and $d^2V/dI^2$ are connected through the relationship:

$$d^2V/dI^2 = -(1/G^3)d^2I/dV^2$$  \hspace{1cm} (11)

Where $G$ is the dynamic conductance that changes slowly over the desired voltage range. If the voltage across the junction is modulated as $V_0 + \delta \cos(\omega t)$, where $\delta$ is the amplitude of the modulating voltage, then current can be written as Taylor series expansion:

$$I(V) = I(V_0 + \delta \cos(\omega t)) = I(V_0) + (dI/dV)_{V_0} \delta \cos(\omega t) + (1/2)(d^2I/dV^2)_{V_0} \delta^2 \cos^2(\omega t) + ... = I(V_0) + (dI/dV)_{V_0} \delta \cos(\omega t) + (1/4)(d^2I/dV^2)_{V_0} \delta^2 (1 + \cos(2\omega t)) + ...$$  \hspace{1cm} (12)

The last term in this expression contains the second harmonic response which is proportional to $d^2I/dV^2$.

Therefore, by detecting the second harmonic of the current in tunnel junction we can extract information about second derivative of the current with respect to voltage.

When at least one of the electrodes is a superconductor, whose electron-phonon coupling is strong the second basic mechanism is observed. The total phonon spectrum, including the superconducting Cooper pairs can be recovered from tunneling density of states $N_r(E)$:

$$N_r(eV) = \sum_{\Delta} \text{Re} \left( \frac{|E|}{[E^2 - \Delta^2(E)]^{1/2}} \right) \frac{\partial}{\partial E} f(E + eV) dE = \frac{(dI/dV)_{s}}{(dI/dV)_{N}},$$  \hspace{1cm} (13)
Where the subscripts $S$ and $N$ indicate whether the electrode is in the superconducting or normal state respectively, $f$ is the usual Fermi function

$$f = \left[1 + \exp\left(\frac{E - E_F}{kT}\right)\right]^{-1},$$

$\Delta$ is the bandgap of the superconductor in BCS theory.

Because of the superconductor bandgap, the current will change once bias voltage will reach value of energy bandgap $\Delta$ (Figure 7). The change in the current will give a step function in the first derivative, and a $\delta$-function in the second derivative. The IET spectrum will have a sharp peak at value $V = \Delta/2$, which can be used to tune in the spectrometer [20].

![Figure 7. Current-voltage characteristic of the normal-superconductor tunnel junction at low bias. Dashed line represents behavior of normal-normal junction.](image-url)
2.10 Resolution of IETS

Peak broadening in IETS is typically in the order of 1 meV ($8 \text{ cm}^{-1}$). There are several factors that influence the width of the peaks in IETS. The two major factors are modulation voltage broadening, and thermal broadening. Modulation voltage broadening is introduced by the modulation voltage applied to measure the second derivative, and thermal broadening is due to thermal smearing of the Fermi function describing the electron distribution. The full width at half maximum (FWHM) for an IETS peak is given by:

$$FWHM = \left[ (1.73eV_{rms})^2 + (5.4k_BT)^2 \right]^{1/2} \text{ (meV)}$$

(14)

where $V_{rms}$ represents the modulation voltage in mV. Using lower modulation voltages will decrease broadening of the peak. However, low modulation voltages will result in low signal to noise ratio, since the signal is related to the magnitude of modulating voltage [19]. Therefore, an optimum modulation voltage must be determined based on the temperature of the experiment. At liquid helium temperature, 4.2K, the thermal broadening is about 1.2 meV. A modulation voltage commensurate with this value is usually employed, since lower voltages will offer little improvement in resolution.

2.11 Spectral Range and Sensitivity

The range for IETS is very broad, depending on the characteristics of the MIM junction under investigation. The lower limit is zero, and the upper limit can exceed 1V ($8000 \text{ cm}^{-1}$) for suitably robust samples. The upper limit can be pushed even further, so that even electronic and optical transitions can be
observed. This spectral range can also provide information on the gap structure of the superconducting metal.

The sensitivity of IETS is high – approximately 0.1% of a monolayer, while the area of the junction can be very small (less than 0.1mm²) [17].

The tunnel current exponentially decays with barrier thickness \(d\) (Table 1), so if the barrier is too thick the tunneling current is too small to detect and the technique fails. Thus, the sensitivity decreases with barrier thickness. Therefore, tunneling spectroscopy is useful in studying only thin (several monolayers) films. It is also useful for quantitative analysis of the number of the molecules contributing to vibrational modes.

2.12 Selection rules

The earliest theoretical treatment of IETS attempting to predict the strength of the peaks and their symmetry was proposed by Scalapino and Marcus in 1967. [21]. In this theory, components of a point dipole and its image normal to the interface which constructs a molecular potential for the tunneling electrons were considered. This potential can be added to the tunneling barrier to calculate the change in the tunneling current. The inelastic current is given by:

\[
j_j^k = \frac{4\pi e^2}{\hbar} \sum_k \sum_j |M_{ij}|^2 f(\epsilon_i) [1 - f(\epsilon_f + eV)] \delta(\epsilon_i - \epsilon_j - \hbar \omega_k)
\]  

(15)

where \(j_j^k\) is the inelastic current due to excitation of the \(k\) th vibrational mode of the molecule with frequency \(\omega\). The matrix element \(M_{ij}\) can be found using WKB-type wave functions.
In order to describe how the intensity of the peaks changes with barrier parameters, Scalapino and Marcus found the ratio of the change in conductance when an inelastic current increases, divided by elastic junction conductance, which is \( \frac{\Delta \sigma^i_k(\rho)}{\sigma_e} \). The factor \( \rho \) is the distance between the molecule with vibrational mode and place, where electron enters the barrier (Figure 8). For the total inelastic conductance one need to integrated over \( \rho \), summed over all vibrations and summed all over all molecules \( n \). The final expression by Scalapino and Marcus:

\[
\frac{\Delta \sigma^i_k(\rho)}{\sigma_e} = \frac{4\pi m e^2}{\phi_0 \hbar^2} \ln \left( \frac{s}{\rho_0} \right) \sum_k \left| \langle k | p_z | 0 \rangle \right|^2 \Theta(eV - \hbar \omega_k), \tag{16}
\]

where \( \phi_0 \) is the barrier height, \( s \) is the thickness of the barrier and \( p_z \) is the component of the point dipole normal to the interface. This expression predicts that only molecules with a net dipole moments perpendicular to the surface will contribute to inelastic current, and this contribution will be proportional to \( p_z^2 \).

In 1968 Lambe and Jaklevic [23] proposed the inclusion of the interactions of the tunneling electron with the induced, as well as intrinsic dipoles of the molecule. The potential due to the effect of the nearest image of a dipole:

\[
V_i^R = -\frac{4\pi \alpha z^2}{(z^2 + \rho^2)^2}, \tag{17}
\]
Figure 8. A schematic diagram of a MIM structure with insulator thickness $s$. A point dipole $p$ and its image are interacting with electron $e$, which penetrates the barrier at a distance $\rho$ from a dipole and is a distance $z$ from the metal electrode. The component of the dipole parallel to the interface cancels with its image.

where $z$ is the coordinate normal to the interface and $\alpha$ is the molecular bond polarizability.

The Scalapino and Marcus expression for inelastic conductance is:

$$\frac{\Delta \sigma^\omega_e(\rho)}{\sigma_e} = \frac{4\pi me^2}{\phi_0} \frac{e^2}{16\hbar^2} \int_0^s \rho^2 \sum_k \left| \langle k|\alpha|0 \rangle \right|^2 \Theta(eV - \hbar \omega_k) \int_0^\rho t(\rho) d\rho$$

Where $t(x) = \frac{1}{x^2} \left[ \frac{1}{1 + x^2} + \frac{1}{x} \tan^{-1}\left( \frac{1}{x} \right) \right]$.

Lambe and Jaklevic showed theoretically that both Raman and Infrared modes should be observed by IETS. Both groups assumed that the electron wave function is localized and a potential was taken for the molecule as a whole.

In 1976 Kirtley, Scalapino, and Hansma (KSH) improved the theory of IETS by introducing a local empirical potential which was the sum of Coulomb potentials due to a set of partial charges localized on the atoms of the molecule:
\[ V_i(\vec{r}) = -\sum_n \frac{e^2 Z_n}{|\vec{R}_n - \vec{r}|} \]  

(19)

where \( e Z_n \) is the partial charge of the \( n \)th atom and \( \vec{R}_n \) is its position [24].

This potential can be expanded to the first order in the atomic positions:

\[ \vec{R}_n(t) = \vec{R}_n(0) + \delta \vec{R}_n(t) \]  

(20)

where

\[ \vec{R}_n(0) = b_n \hat{x} + c_n \hat{y} + a_n \hat{z} \]  

(21)

\[ \delta \vec{R}_n(t) = \delta \vec{R}_n(0)e^{i\omega t} \]  

(22)

This allows the potential to be rewritten in terms of local dipoles

\[ V_i(\vec{r}) \approx -\sum_n e^2 Z_n \delta \vec{R}_n \nabla_n \left( \frac{1}{|\vec{r} - \vec{R}_n|} \right) e^{i\omega t} \]  

(23)

where \( e Z_n \delta \vec{R}_n \) is the dipole moment.

When calculating the potential, one must include the multiple image charges on each electrode:

\[ V_i(\vec{r}) = \sum_{k=-\infty}^{\infty} \sum_n \frac{e^2 Z_n \delta \vec{R}_n}{\varepsilon} \nabla_n \left( \frac{1}{|\vec{r} - \vec{R}_n - 2ps\hat{z}|} - \frac{1}{|\vec{r} - \vec{R}_n - (2ps - 2a_n)\hat{z}|} \right) e^{i\omega t} \]  

(24)

where \( \varepsilon \) is the dielectric constant of the barrier.

KSH theory uses the zeroth-order Hamiltonian with the potential mentioned above and WKB wave functions to find the expression for the change in conductance through the transfer matrix elements:

\[ M_{ij} = \int_{-\infty}^{\infty} d^3x \psi_j^* V_i(\vec{r}, \vec{R}) \psi_i \]  

(25)
The final result:

\[
\Delta \sigma = \frac{8\pi e^2}{\hbar} \left( \frac{L}{\pi} \right)^6 \left( \frac{m}{\hbar^2} \right) \left( \varepsilon_f \right)^{1/2} \left( \varepsilon'_f - eV \right)^{1/2}
\]

\[
\times \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \int_0^1 d((\cos(\theta)|M_{y}\rangle|^2 \Theta(\hbar \omega_k - eV)
\]

(26)

Where \( L \) is a normalization factor, \( \varepsilon_f \) and \( \varepsilon'_f \) are the Fermi energies of the electrodes.

KSH theory predicts the intensities for both Raman and infrared modes observed by IETS, which are in reasonable agreement with experiment. There is another observation that vibrational modes couple more strongly with tunneling electrons if their net dipole moment is normal to the surface. The physical interpretation is that the dipole moments parallel to the interface cancel out with their image, but for the dipole deep within the tunnel barrier that is no longer true. Therefore, there still exists a small probability of excitation for the dipole parallel to the surface deep within the tunnel barrier. Tunneling spectroscopy can also detect modes that are forbidden for both Raman and infrared. KSH theory is based on interaction potential, which contained only the intrinsic oscillating dipole potentials.

2.13 Raman Spectroscopy

Raman spectroscopy is a probe for investigating vibrational modes of adsorbed molecules. Its based on Raman the process – inelastic light scattering by molecular vibrations [24].
Raman spectroscopy has a number of advantages, such as very high resolution, very low scattering profile, and can be perform in ambient conditions. It can be used on a wide variety of surfaces and substrates including oxides (such as Al oxide).

Of particular relevance to the present work is a Surface-Enhanced Raman Spectroscopy (SERS). The Raman signals are enhanced a many times if interacting molecules are adsorbed on certain metals. The enhancement factor can be as large as $10^6$. The reasons for such a great change are not fully understood. [25], [26].

2.14 Classical theory of Raman Scattering

When a molecule is irradiated with a laser source approximately 0.001% can be scattered either elastically or inelastically. The elastical component is referred to as Rayleigh scattering, and the inelastical – Brillouin or Raman scattering. The electric field of the light induces a dipole moment in the molecule that scatters the light. The appearance of the dipole moment arises from the polarizability of the bonds in the particular molecule. Rayleigh scattering corresponds to static polarizability, while a change of polarizability by electronic, rotational or vibrational motion leads to Raman scattering. Brillouin scattering is caused by interaction of the light with acoustical waves and is not of interest of Raman spectroscopy.

Classically, the electric field of the incident light [24]:

$$\vec{E} = \vec{E}_0 \cos(2\pi v_0 t)$$  \hspace{1cm} (27)
with $\nu_0$ being the frequency of the light.

The electric field induces a dipole moment $\mu$, in the molecule:

$$\tilde{\mu} = \tilde{\alpha}\,\tilde{E}$$

(28)

where $\tilde{\alpha}$ is the polarizability of the molecule modulated at the vibrational frequency $\nu_1$:

$$\tilde{\alpha} = \tilde{\alpha}_0 + \tilde{\alpha}_0 \cos(2\pi\nu_1 t)$$

(29)

Combining (27), (28) and (29):

$$\tilde{\mu} = \tilde{\alpha}_0 \tilde{E}_0 (1 + \cos(2\pi\nu_1 t)) \cos(2\pi
u_0 t) =$$

$$= \tilde{\alpha}_0 \tilde{E}_0 \cos(2\pi\nu_0 t) + (1/2)\tilde{\alpha}_0 \tilde{E}_0 \cos(2\pi(\nu_0 + \nu_1) t) + (1/2)\tilde{\alpha}_0 \tilde{E}_0 \cos(2\pi(\nu_0 - \nu_1) t)$$

(30)

When looking at a spectrum (Figure 9) of scattered light one can see three bands: unchanged frequency $\nu_0$ (Rayleigh scattering), a $\nu_0 + \nu_1$ peak (anti-Stokes Raman scattering), and a $\nu_0 - \nu_1$ peak (Stokes Raman scattering). The following model describes the selection rules for Raman spectroscopy. The electric field of the incident light may induce a dipole moment in a molecule that is not parallel to the applied field, because of particular symmetry of molecular electronic distributions. Therefore, polarizability is a tensor and related to induced dipole moment through the relationship:

$$\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}$$

(31)

For nonresonant Raman scattering, the polarizability tensor is real and symmetric. For resonant Raman scattering, the polarizability tensor may have
Figure 9. Schematic diagram of a Raman spectrum. Three bands are present: an unchanged frequency $v_0$ (Rayleigh scattering), a $v_0 + v_1$ peak (anti-Stokes Raman scattering), and a $v_0 - v_1$ peak (Stokes Raman scattering).

imaginary components. For the real polarizability tensor the induced dipole can be calculated, since it can be diagonalized. The polarizability ellipsoid provides visualization of molecular polarizability in either the magnitude or the direction.

Molecular vibrations are Raman active if they cause a change in a component of the molecular polarizability.

The effect of sample size on Raman line shift becomes noticeable, when the dimensions of nanocrystals come into play. In order to estimate the impact of the size, a macroscopic treatment of optical phonons in a small spherical crystal can be used [27], [28]. A more detailed consideration is included in Appendix.
2.15 AFM principles

Surface imaging and analysis have changed dramatically since the development of the atomic force microscope (AFM) in 1986 [29]. AFM has found numerous applications in surface imaging, manipulation and biological studies [30], [31], [32], [33].

The technique of Atomic Force Microscopy relies upon sensing the force exerted between a sample and a very sharp tip mounted on a cantilever. This is done by measuring the deflection of the cantilever (Figure 10(a)). A sample is moved under the tip and the cantilever deflection is measured by an optical lever, which corresponds to the force associated with the tip-surface interaction (Figure 10(b)). One of the forces that contributes into this interaction is an interatomic van der Waals force. There are two regions of interest: one is when the tip and surface are in close proximity (contact mode) and the force is negative or repulsive, and another when the tip and surface are further apart (non-contact mode) and the force is attractive.

In the contact mode regime, there are two possible ways of obtaining an image of the surface: constant-force and the constant-height modes. In constant-force mode, the tip probes the surface while the force of “contact” is held constant, and monitored, using an optical system and a feedback mechanism, utilizing a piezoelectric nano-actuator. The piezoelectric deflection is then plotted versus displacement of the sample in the plane of the surface, resulting in constant force lines. This is a fast way to image the surface, since the scanning time is limited only by the response time of the feedback circuit. In constant-
Figure 10. AFM measurements principles. (a) Schematic diagram illustrating the basics of AFM measurement principles. (b) Samples under investigation are moved by a piezoelectric actuator controlled by a feedback circuit from a reflected laser beam and optical detector associated interaction potential between a typical AFM tip and the surface of interaction between tip and surface.
height mode the separation between the tip and the sample is held constant and the topographic image is obtained by scanning in a similar manner. The image now represents the force variation between the tip and surface.

In the non-contact regime, an AFM cantilever oscillates at its resonant frequency near the surface of the sample. The separation between the tip and the surface is of the order of tens of angstroms and the dynamics of interaction is on the right side of the van der Waals curve. The attractive force between the tip and the surface is much smaller than in contact mode, and in order to measure changes in this force a sensitive AC detection scheme must be used. The feedback circuit now monitors the resonant frequency of the cantilever and keeps it constant by adjusting the tip-surface separation. Non-contact mode has advantages over other methods for soft samples or samples that are easy to damage, since, essentially, the sensitivity is greater.

AFM-assisted surface oxidation and modification has been a technique considered for nanofabrication and nanoelectronics [32], [33], [34]. It has been shown that, using nanolithography, it is relatively easy to fabricate a field effect transistor [35], gate transistor [36], and a waveguide division multiplexing [37]. There are several different methods of oxidation such as DC voltage oxidation [34], non-contact AFM surface anodization [38], AC voltage modulation techniques [39], [40] and a relatively new method AFM-assisted electrostatic nanolithography (AFMEN), on polymer films [32], [41], [42], [43]. This technique generates features on uniform polymer thin films within an initially uniform, planar film without chemical crosslinking. AFMEN is a combination of localized softening
of the polymer by Joule heating, polarization by an extremely non-uniform electric field, and manipulation of softened polymer. The main idea of this technique is to heat a polymer film locally with AFM above the glass-transition temperature and then, using the strong electric field near the tip apex polarize the dialectic polymer and electrostatically attract it to overcome Laplacian pressure. AFMEN allows a creation of nanostructures as small as 5-50 nm wide and 1-100 nm high. Modified polymer films are easy to produce but they undergo time and temperature degradation.

The electrochemical processes involved in modifying the surface are not fully understood, despite the number of techniques capable of modifying the surface. According to Dagata’s, Garcia’s and Lyuksyutov’s groups (Figure 11) the processes of oxidation on Si surface are governed to the two chemical reactions:

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{Si} - 4\text{e}^- + 2\text{OH}^- \rightarrow \text{SiO}_2 + 2\text{H}^+ 
\]

A sharp conductive tip creates high electric field that causes dissociation of ambient water. The abundance of electrons that are created by the first reaction is responsible for the current through a water meniscus between the tip and surface. Hydroxyl ions react with silicon resulting in a silicon oxide on a surface. The speed of growth of silicon oxide is limited by the availability of hydroxyl ions and their mobility through already oxidized regions on the surface. The current in this regime has Faradiac character and mainly depends on migration of the hydroxyl ions. The water meniscus present between the tip and surface and the size (50 nm). The height of the structures formed are of order 2.2nm - typical for
Figure 11. Schematic representation of an AFM tip-surface junction. A sharp conductive tip creates high electric field that causes dissociation of water. The anomalous current is associated with an avalanche breakdown in the part of the space-charge layer inside the water meniscus and also inside the semiconductor in which a large number of electron–hole pairs is generated. Competition between recombination of electrons and holes, and the variation of field-induced hole concentration results in regions of depleted holes. OH\textsuperscript{−} ion distribution follows the distribution of the hole concentration, which leads to oxide growth in the areas where the concentration is maximal, and therefore in the formation of oxide rings [44].

the assisted oxidation of silicon (Figure 12 (a)).

At a certain voltage, electrostatic breakdown may occur, resulting in a field induced ionization of the water in the meniscus. The ionization of water yields a number of electrons capable of traveling through the meniscus. The effective density of the field-induced holes near the interface increases as the normal component of the electric field increases. The electron density inside the
meniscus is proportional to the strength of the electric field, which decreases with the distance from the tip apex. Competition between the recombination of electrons and holes, and the variation in the field-induced hole concentration results in the areas without holes, preventing the formation of the space charged layer and resulting in the similar pattern of hydroxyl ion distribution on the surface. The result of this is the ring type structures (Figure 12 (b,c)) [44].

Figure 12. AFM contact mode images of oxide structures produced on a n-silicon surface (a) tip voltage $V = -5$ V, and measured current $i < 0.1$ nA, below the breakdown; (b) $V = -20$ V, $i = 250$ μA, breakdown; (c) $V = -45$ V, $i = 400$ μA, above the breakdown. The formation of an additional ring is associated with oxide growth in the areas of maximal hole density [44].
3.1 IETS sample preparation

Samples were prepared on precleaned glass microscope slides, in a high vacuum system (modified Denton Vacuum DV-502A). The vacuum system has a stainless steel vacuum chamber and a base pressure of $10^{-7}$ Torr. It has capabilities for thermal evaporation, RF, and DC sputtering, plasma discharge and manipulation of samples over these deposition sources using shutters and shadow masks. Prior to each sample fabrication, the chamber and RF sputter source were cleaned with an argon plasma discharge. Next, Al electrodes were evaporated onto the glass substrate. Depending on the required tunnel barrier, one or more of the following procedures were followed:

(a) The sample was removed from the chamber and spin doped with solvent. This procedure was employed to ensure there is no contamination in the chamber or solvent.

(b) RF sputtering of CdS in a background of argon with chamber pressure $\sim 50$ mTorr. A 2 in. diameter 0.25 in. thick 99.999 % pure CdS sputter target, supplied by Kurt J. Lesker Company, was used. Deposition rates were in the range 0.01-0.02 nm/s. The thickness of CdS films was 3nm determined by a quartz film thickness monitor. (The rate of deposition
and the gas pressure were chosen after an AFM study of samples to ensure the most uniform coverage and minimize the roughness of the surface)

(c) First a CdS film was sputtered as described in (b), then the film was spin doped with compound 7-Ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane (7ETTD) [46] [47] dissolved in dichloromethane and diethylether in the following proportion: 9 mg 7ETTD/2 mL Dichloromethane/13 mL Diethylether. Such a solution was found to produce more uniform surface coverage of the adsorbate as indicated by tunnel junction resistance measurements.

(d) Liquid phase doping of CdS doped with an aqueous, acidic hydrolyzed triethoxisilane solution. This was achieved by placing one or two drops of the solution onto sample, and spinning off the excess. The solution was prepared previously by first adding two drops of HCl and then 50 μL of TES to 100 mL of ethanol, and then finally adding 100 μL of water to avoid polymerization of the TES. This procedure results in the hydrolysis of the TES by the following mechanism

\[ \text{HSi(OC}_2\text{H}_5)_3 + 3 \text{H}_2\text{O} \rightarrow \text{HSi(OH)}_3 + 3\text{C}_2\text{H}_5\text{OH} \]

(e) The CdS film was doped with a 0.05 mg/mL solution of PMMA in acetone.

(f) The film was doped with a 0.1 mg/mL solution of polyaniline in DMF. To complete the fabrication process, tunnel junctions were capped with an approximately 300 nm thick lead cover-electrode. We used 99.999% pure or
better source materials for both aluminum and lead. Figure 13(a) shows a schematic diagram of the sample geometry.

Both aluminum and lead electrodes were evaporated at a pressure in the range 10\(^{-7}\) to 10\(^{-6}\) Torr, from a heated tungsten filament or alumina crucible. Shadow masks with appropriately oriented slits were used to pattern the required electrode geometry to facilitate voltage and current measurements via a four probe measurements system (Figure 13 (b)). The junction area is approximately 1 mm\(^2\).
Figure 13. Schematic diagram of an Al/CdS/adsorbed layer/Pb tunnel junction. (a) Geometry from the side. Geometry of tunnel junction structure fabricated on a glass substrate from the top. (b) The junction location is indicated and has an area of 1mm².
3.2 I-V and conductance-voltage (G-V) measurements

Four terminal I-V measurements were performed, and the data were recorded using code written using a commercially available data acquisition software package. Conductance-voltage (G-V) data were derived numerically from I-V measurements, by taking the derivative of the data, using a finite difference algorithm. Measurements were performed in a cryostat at temperatures in the range 4.2-298 K. The temperature was measured using a Si tunnel diode temperature probe (CY7 purchased from Omega Technologies Company).

3.3 IETS measurements

A schematic representation of the in-house built IET spectrometer is shown in Figure 14 [47]. Its operation is as follows. The digital to analog converter (DAC) provides the dc bias voltage across the junction. The digital multimeter (DMM) is used to measure the bias voltage and also the ac modulation voltage. The lock-in amplifier (LIA) is used to provide the modulation signal reference and to measure the second harmonic of the fundamental.

The mixer circuit is used to combine the dc voltage and the modulation voltage and to isolate the source impedance. The computer is used as a system controller and for data acquisition and processing purposes. The signal regulator provides constant resolution mode by ensuring the modulation voltage across the sample is held constant [47].

Spectra were recorded with samples cooled to 4.2 K in liquid helium. Low bias features of the Pb superconducting band gap were recorded to verify that
tunneling is occurring. Normalized tunneling intensity spectra were recorded in constant resolution mode [47] with a modulation voltage of 1mV. The modulation frequency was set at 50 kHz, to minimize 1/f noise, the dominant source of the noise in the system. Each spectrum was recorded by signal averaging over 20 or more scans.

3.4 Raman measurements

Dr. Sokolov’s group (The University of Akron, Polymer Science) kindly provided their help and equipment (listed below) with Raman measurements. For samples prepared in our lab Raman spectra were collected using an in-house built AFM-tip enhanced nano-Raman spectrometer [48]. The instrument relies on the enhancement of the Raman signal by an incident laser beam which impinges
on the sample through a long working distance objective. The electric field of the incident beam is locally enhanced at the point of contact between the modified SPM tip and the sample. The detector consisted of a Horiba/Jobin-Yvon monochromator Labram HR800 with a nitrogen-cooled CCD camera. The elastic line was suppressed by a 647nm notch filter. Optical system: the sample was illuminated by a 514.5 nm Lexel laser through a Mitutoyo long-range-working objective (x50, N.A. 0.42).

3.5 FTIR measurements

A Mattson Cygnus 100 model 7020A FTIR spectrometer with a mercury cadmium telluride detector was used to collect spectra. The samples for FTIR measurements were prepared in the same way as for the IETS, with couple of exceptions. There were no top metal electrodes and the geometry of the slides was different, since no electrical connection needed to be made.

An in-house modified Multiple Reflection Absorption Infrared Spectroscopy (MRAIRS) technique was used to record IR spectra of the samples, of surfaces covered with the molecules of interest. Such a spectrum can give a detailed information about the geometry of the adsorbed molecules [49] [50] [51].

A modified attenuated total reflection module (ATR) manufactured by Specac Ltd., was used to perform the MRAIRS measurements (Figure 15). The first set of mirrors converge the infrared beam on a sample holder with a sample, and after multiple reflections inside, another set of mirrors collects the beam and redirect it into the detector. The sample holder contains two glass slides, with one
being a little longer than the other for entry and exit of the infrared beam. There are two factors in competition for determining the optimum number of reflections. First, the more reflections that occurs the more chances to loose energy to excite the specific molecular vibration and obtain better the signal-to-noise ratio. On the other hand, at near grazing angles of incident the reflectivity of a metal decreases and the intensity of the beam decrease very rapidly. The signal-to-noise ratio is proportional to $\Delta R(N, \theta)$, the difference in reflectivity between that of the bare metallic substrate $R_0$ and the metal substrate with a thin absorbing layer $R$. $N$ is the number of reflections and $\theta$ is the angle of incidence. In order to find the optimum angle one must consider the reflection ratio $-N \log \frac{R}{R_0}$ as a function of incident angle. The maximum corresponds to angle of 60 degrees.

The number of reflections depends on an angle of incident:

$$N(\theta) = \frac{l \cos(\theta)}{d}$$

(32)

where $l$ is the mirror length, $d$ is the distance between the mirrors. For our ATR mount: $l = 5.2\,cm$; $d = 0.2\,cm$ and $\theta = 60^\circ$. The optimum number of reflections is thirteen.

The orientational selection rules of MRAIRS allow us to interpret the spectral data to determine molecular geometry at the adsorbate/surface interface. Upon reflection on the surface, the components of the incident light polarized parallel to the plane of incidence (p polarized) has a different phase shift than light polarized perpendicular to the plane of incidence (s polarized). For the p component the phase shift is 90 degrees and the s component has a shift
of 180 degrees. As the result the s-polarized light will have an electric field 0 at the surface and therefore will not excite any vibrational modes. Since there was no useful information about the surface with this component, to improve the signal-to-noise ratio it was eliminated by using a polarizer.

Figure 15. Modified ATR attachment. (a) Top view of the FTIR spectrometer (b) Sample holder for MRAIRS.
3.6 AFM imaging

A Veeco Metrology Digital Instruments 3100 Dimensions AFM employing a Nanoscope IV controller was used in this study. The instrument was housed in a class-100 clean room. A non contact, highly conductive Micromash NSC12 ultrasharp cantilever, 90μm long and 35μm wide, with a force constant of 5 Nm\(^{-1}\), was mounted on an in-house modified tip holder isolated from the rest of electric circuits by a piece on insulating spacer. The motion of a piezoelement embedded in the tip-holder with a resonant frequency of 240–315 kHz was controlled using C++ code combined with a Digital Instruments nanolithography package, and this was used to manipulate the AFM tip through the following steps (Figure 16):

(a) the tip was brought towards the surface to a distance where the vibration amplitude (varied between 0.5 and 3.0 V) was suppressed by three orders of magnitude. An oscilloscope was used to monitor the tip’s vertical deflection signal. The tip-surface separation for this event was selected as the reference point.

(b) the tip, while oscillating, was raised to point \(A\) varied between 10 and 50 nm.

(c) a bias voltage, in the range of \(-10\) to \(-40\) V, was applied to the tip, to a which was the slowly retracted to point \(B\), varied between 150 and 400 nm. The retraction speed varied from 50 to 200 nm s\(^{-1}\) which allowed for a total exposure time of 0.5–2 s.
(d) the fourth step was lateral displacement of the tip, to a distance varied between 300 and 500 nm, and back to the reference point. The cycle was then repeated to create more nanostructures.

Schematically, this simple protocol named z-lift amplitude modulated (ZAM) AFMEN is presented in Figure 16 [52].

Figure 16. Schematic representation of the four-step ZAM protocol. First, a weakly biased AFM tip is brought towards the surface of the a-CdS film whose thickness was in the range of 30–500 nm. Second, the tip is held at reference point A. Third, the AFM cantilever, oscillating at 240–330 kHz, is slowly retracted from point A to point B while simultaneously applying a bias voltage of −10 to −40 V: this step forms the nanostructures, 8–40 nm high and 50–150 nm wide, on the a-CdS surface. Bottom: Three dots formed using an exposure time of 2 s; the AFM tip was z lifted from 50 to 250 nm and the tip bias was −30 V [52].
3.7 Electric Force Microscopy (EFM) imaging

EFM is an established experimental method for local observations and measurements of charge distributions on semiconductors [53] [54]. Electrical forces between a conducting AFM tip and the surface act as a second order effect on mechanical vibrations of the tip. Assuming there is a potential difference between the tip and the surface, the mutual force between them is given by

$$F = \frac{1}{2} \frac{dC}{dz} V^2$$

(33)

where C is the surface-tip capacitance, and V is the applied voltage. The applied voltage has several components:

$$V = (V_{cp} + V_{dc} + V_{induced}) + V_{ac} \sin \Omega t$$

(34)

where $V_{cp}$ is a contact potential, $V_{ac}$ and $V_{dc}$ are the applied dc and ac voltages respectively, and $V_{induced}$ is related to induced voltages between the tip and the surface. As a result, the tip-surface force will have constant and oscillatory components, $F_{dc}$ and $F_{\Omega}$, respectively given by

$$F_{dc} = \frac{1}{2} \frac{dC}{dz} \left[ (V_{dc} + V_{cp} + V_{induced})^2 + \frac{1}{2} V_{ac}^2 \right],$$

(35)

and

$$F_{\Omega} = \frac{dC}{dz} \left[ (V_{dc} + V_{cp} + V_{induced}) V_{ac} \right] \sin \Omega t.$$  

(36)

The second term $F_{\Omega}$ has a linear dependence on the capacitance coupling $\frac{dC}{dz}$ and sample voltages. If a voltage is applied such as that $F_{\Omega} = 0$, surface voltage variations can be measured and imaged. If one is interested in surface charge, $F_{\Omega}$ can be observed. An additional Coulomb force appears
between the static charge \( Q_s \) of the sample and the ac charge induced on a tip and the oscillating force component becomes

\[
F_\Omega = \left[ \frac{dC}{d\Omega} \left(V_{dc} + V_{cp}\right) - \frac{QC}{4\pi\varepsilon_0 z^2} \right] V_{ac} \sin \Omega t. \tag{37}
\]

An in-house modified electric force microscopy EFM [52] was used to monitor the electric charge distribution and its sign at the sample surface (see Figure 17). In our system a sweep function generator was used to apply a 25–30 kHz sinusoidal modulation reference signal with an amplitude of 4–5 V rms to the AFM tip, and a digital lock-in amplifier was employed to recover the tip’s vertical deflection. It is assumed that the associated electrostatic force due to the modulation signal has a negligible effect on the mechanical oscillations of the tip at 250–300 kHz. The patterned nanostructures thus formed were imaged and their topography and electric charge distribution at the surface were recorded over a period of several seconds after the ZAM protocol was completed.
Figure 17. Block diagram of the electric force microscopy EFM technique. To reduce unwanted noise, an ac modulation signal 25–30 kHz, 4–5 V rms is applied to the tip and the vertical deflection response signal which contains information of surface electric potential is recovered using a lock-in amplifier. The image is collected 30 s after the ZAM protocol is completed [52].
3.8 7ETTD synthesis

The synthesis of 7ETTD was performed by Dr. Hu’s research group as follows [55]. Sodium hydride (60 mg, 1.4 mmol, 60% dispersed in mineral oil) was dispersed in dry toluene (10 mL) in a round bottom flask which was equipped with a magnetic stirrer and cooled in an ice bath. (2-oxo-propyl)-phosphonic acid dimethyl ester (22 mg, 1.3 mmol) was added slowly. The solution mixture was stirred for an additional hour after the addition. A solution of methanesulfonyl azide (17 mg, 1.4 mmol) in a mixed solvent of toluene and THF was added to the above reaction mixture. The resulting reaction mixture was allowed to slowly warm up to ambient temperature and stirred for additional 2 hours. The reaction mixture was filtered through a celite filter cake to give yellowish oil of (1-diazo-2-oxo-propyl)-phosphonic acid dimethyl ester, which was used for the next step without further purification.

To a stirred solution of oxalyl chloride (0.07 mL, 0.83 mmol) in 3 mL in 4 mL dichloromethane in a three necked round bottom flask (25 mL) was added dimethyl sulfoxide (0.12 mL, 1.66 mmol) dropwise through a dropping funnel while the reaction temperature was maintained at -78 C for additional 5 minutes after the addition. A solution of (2,4,9 – trithia-tricyclo[3.3.1.1³,7]dec-7-yl)-methanol (240 mg, 1.09 mmol) in 5 mL of dichloromethane and was added dropwise to the above reaction mixture. After, the reaction mixture was stirred at -78 C for 45 minutes (reaction monitored by TLC), and triethylamine (5 mL) was added. The resulting reaction mixture was allowed to warm up to room
temperature while stirring. The reaction was quenched with water (20 mL) and extracted with dichloromethane three times (3 x 10 mL). The crude product was obtained after removing the solvent under reduced pressure.

To a mixture of aldehyde in 2 mL of dry methanol and potassium carbonate (0.63 mg, 2.0 mmol), the solution of (1-diazo-2-oxo-propyl)-phosphonic acid dimethyl ester (1.2 equivalents) in dry methanol was added. The resulting reaction mixture was stirred for 12 hours at room temperature. The reaction mixture was diluted with dichloromethane (20 mL) and extracted with additional portions of dichloromethane (2 x 20 mL). The combined organic layers were washed with sodium bicarbonate. After evaporation of the solvent, the crude product was purified by column chromatography to yield 7-Ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane [55].

3.9 CdS nanoparticles synthesis

The synthesis of the nanoparticles was performed with Dr. Hu’s research group, using an aqueous precipitation method developed by G. A. Martinez-Castanon [56]. CdSO_4 x2.5H_2O was dissolved in 1L of deionized water to a concentration of 2 mM. While stirring, 1.94 g of 1-thioglycerol was added and the mixture was stirred for additional 5 minutes. Ammonium sulfide (30 mmol) was rapidly added under ambient conditions to form cadmium sulfide nanoparticles.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Control Spectrum

Figure 18 shows control IET spectra obtained from (a) Al/CdS/Pb, (b) Al/CdS/solvent/Pb, and (c) Al/alumina/solvent/Pb junctions which display acceptable trace amounts (sub-monolayer) of hydrocarbon contamination. The control spectrum (a) is presented to illustrate peaks normally seen for CdS samples and there is some evidence of Al-O as evident by the phonon peak in the spectrum at 980 cm\(^{-1}\). Peaks due to CdS appear as a shoulder at 1110 cm\(^{-1}\) and a smaller feature at 236 cm\(^{-1}\) but these peaks cannot be assigned with confidence to particular CdS modes. Spectrum (b) has a broad peak c.a. 1100 cm\(^{-1}\) due to CdS, and another broad peak c.a. 720 cm\(^{-1}\) due to bending of surface hydroxyl modes. It has no other discernable features. This spectrum indicates that the solvent neither reacts nor adsorbs on the CdS surface. The peaks present in spectrum (c) are: an Al metal phonon at 300 cm\(^{-1}\), Al-O phonon vibrations c.a. 980 cm\(^{-1}\), a broad peak at 3730 cm\(^{-1}\) due to stretching of Al-OH, and C-H stretching modes c.a. ~3100 cm\(^{-1}\). Note also the rising background in Figures 18 (c) and 18 (b). These indicate that the barrier parameters has been modified and this aspect will be discussed in section 4.2.1.
4.2 7ETTD

In this work, we present data on the adsorption of the new compound 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1³⁷]decane (7ETTD) (Figure 19) on an ultrathin-film (6 nm) CdS surface [57]. We will show that the compound adsorbs on a the surface by orienting in such a way to form a heterojunction and will investigate the electronic properties of these heterojunctions. Their current-voltage dependences are recorded over a temperature range of 4.2K to 300K. Conductance-voltage \( G(V,T) \) and data derived from those measurements allow us to determine the associated conductance mechanisms in the heterojunctions. Inelastic electron tunneling spectroscopy (IETS) is also used to characterize the electronic properties of the junctions. IETS has been shown to be a useful tool for

![Figure 18. Control IET spectra obtained from (a) Al/CdS/Pb, (b) Al/CdS/solvent/Pb, and (c) Al/alumina/solvent/Pb junctions.](image)

\[ \text{Intensity (arbitrary units)} \]

\[ \text{cm}^{-1} \]
Figure 19. Model of 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane (7ETTD). (a) Structural model of 7ETTD (b) Schematic cross section of an Al/CdS/7ETTD/Pb tunnel junction. The Al and Pb films are approximately 100 and 300 nm thick respectively and the CdS layer 3 nm. The 7ETTD molecules are approximately 0.6 nm long as determined by Gaussian 98 B3LYP/6-31+g(d,2p) calculations [63].
investigating physical phenomena on surfaces. It has been used previously to study vibrational spectra of ultrathin sputtered films of germanium oxide, silicon and its oxides and also CdTe oxides [58] [59] [60]. As mentioned previously IETS has an intrinsic advantage over IR and Raman spectroscopy for surface analysis since the signal to noise ratio increases for thinner film, such as those under investigation in the present work. IETS has been shown to be a convenient technique for investigating tunnel barrier parameters for thin layers of semiconductors [60] [61] [62].

4.2.1 Conduction mechanisms

Different conductance mechanisms are possible in MIM structures, these include direct tunneling, Fowler-Nordheim tunneling, hopping, and others. In order to verify which mechanisms predominate at various I, V, and T values, we analyzed the temperature dependence of corresponding conductance-voltage measurements. Figure 20(a) and 20(b) show $G(V,T)$ dependences for an Al/CdS/Pb junction and an Al/CdS/Pb junction modified with (7ETTD) respectively. The $G(V,T)$ surface maps of these two junctions are significantly different, indicating that different conduction mechanisms are at play in different regions. (Notice also that Figure 20(a) exhibits a more significant bias polarity dependent asymmetry as compared to Figure 20(b). This is believed to be due to modification of the barrier parameters and conduction mechanisms when the 7ETTD layer is introduced and will be discussed further. Pb superconducting energy gap structure is present at low bias for both type of junctions, indicating
Figure 20. Temperature dependent conductance-voltage plots for (a) an
Al/CdS/solvent/Pb tunnel junction, and (b) an Al/CdS/7ETTD/Pb tunnel junction.
Introduction of the 7ETTD layer reduces the degree of bias- and temperature-
dependent asymmetry and increases the relative range of normalized
conductance [57].
that a tunneling mechanism is present, but has been removed from the figures for clarity. It is logical to assume that, at low voltages and temperatures, direct tunneling will be the dominant mechanism. Indeed, for direct tunneling, the current is proportional to voltage as we observe and there is no temperature dependence for either type of junction. Calculations of the barrier parameters will be presented later. For hopping, the current density is given by \( J \sim V \exp\left(-\frac{\phi}{kT}\right) \), where \( \phi \) is the defect activation energy and \( k \) is Boltzmann’s constant. Figure 21 shows plots of \( \ln G \) versus \( 1/T \) for a Al/CdS/Pb junction at various bias voltages in the range 0 to 0.5 V. The slope of the plots at low values of \( 1/T \) (i.e. sufficiently high temperatures) should approach linear behavior, if hopping conductivity exists, allowing \( \phi \) to be determined from the slope of this linear region. However, we do not observe purely linear behavior so cannot unequivocally determine a value for \( \phi \). We should point out that we also observe similar \( \ln G \) versus \( 1/T \) behavior for junctions with adsorbed 7ETTD molecules, which indicates that the behavior is not associated with the molecules alone, but rather with the CdS interface.

If the bias voltage approaches the barrier height \( \phi \), one would expect to observe Fowler-Nordheim tunneling. However, neither junction displays Fowler-Nordheim conduction. This indicates that for the bias range under investigation (approximately 0 to 0.5 V) we do not approach the Fowler-Nordheim region and another conduction mechanism must exist which would explain the difference.
Figure 21. Bias dependence of $\ln(S)$ versus $1/T$ for an Al/CdS/Pb junction.

between the conductance of doped and unmodified junctions at the high end of our bias range (above ~ 0.2 V).

One such mechanism is the transport of electrons through localized channels created by doping. Gaussian 98 B3LYP/6-31+g(d,2p) calculations [63] were performed and yield a value of ~ 5.8 eV for the HOMO LUMO gap of the 7ETTD molecule, which is too large to reduce the bandgap of the CdS layer and increase the conductance. A frontier orbital model has been proposed to explain band bending and surface charge accumulation on passivated GaAs surfaces.
We suggest a similar mechanism may be responsible for the observed behavior of the CdS/7ETTD heterojunctions. Figure 22(a) shows the traditionally accepted explanation for coupling between HOMO and LUMO levels for two interacting molecules which occurs to minimize the electronic energy of the system, and is included for illustration purposes. Figure 22(b) schematically represents the frontier orbital model proposed for the explanation of the modification of the surface of a n-type semiconductor and the argument is as follows. The interaction of the LUMO of the adsorbate and the HOMO of the semiconductor (in this case occupied by electrons bound to surface states) forms a new LUMO high above the Fermi level and a new HOMO surface state down in the valence band. The created states behave as new channels that raise the conductance of the junction. Lowering the energy of the surface states causes electrons to be delocalized in the valence band, which reduces the net charge on the interface. Electrons are no longer trapped at the surface, as was the case with an unmodified semiconductor. Reducing the charge of the surface automatically reduces the band bending, which ultimately leads to a reduction of the effective barrier height. For p-type semiconductors the majority carriers are holes, and surface states are now located above the Fermi level near the conduction band. Now surface states play the role of LUMO levels in HOMO-LUMO interactions, since they are empty because of the location above the Fermi level. When the surface is interacting with molecules those states are pushed towards the conductance band edge, which decreases the positive charge traps on the surface. The CdS used in the experiment is undoped.
Figure 22. MO Diagrams of molecular interactions (a) Conventional MO Diagram of a HOMO-LUMO molecular interaction. (b) MO diagram indicating interaction between surface states of CdS and an adsorbed 7ETTD molecule.
Because it is assumed that both types of surface states are present in equal amounts, both the HOMO and the LUMO levels are participating in creating conduction channels.

The strength of the coupling between molecular orbitals and surface states depends on their mutual location. The greater the energy separation of the levels the smaller interaction will be.

4.2.2 Model barrier parameters calculations

As mentioned in 4.2.1, at low bias and temperature the $I$-$V$ curve is linear to a very good approximation. However, for higher voltages the dependence becomes exponential. We employed a WKB approximation to calculate the normalized low-bias (from 0 to ~ 0.2 V) conductance for an assumed composite (trapezoid + square, or TRAPSQR) barrier corresponding to CdS and alumina components respectively (see Figure 23). The calculated normalized conductance was fitted to the experimental conductance data. As mentioned earlier, the $G$-$V$ data was obtained from experimental $I$-$V$ data by numerical differentiation. A standard least-squares function, from a commercially available software package (MATLAB), was used to perform the fitting. The WKB approximation assumes the following expression for tunnel current density:

$$j = \frac{2e}{\hbar} \int \exp \left( -\frac{2}{\hbar^2} \int_0^d \left[ 2m [\phi(x, V) - E_s] \right]^{1/2} dx \right) \times \left[ f(E) - f(E - eV) \right] dE_s$$ (38)

where the $\hbar$ is Planck’s constant, $\hbar = h / 2\pi$ , $e$ is the electronic charge, $x$ is the distance into the barrier, $d$ is the total thickness of the barrier, $E$ is the total
Figure 23. TRAPSQR barrier used for WKB approximation. \( \phi_1, \phi_2, \) and \( d \) represent the barrier heights and thickness respectively associated with the CdS layer, while \( \phi_3 \) and \( s \) are the barrier height and thickness for an assumed present alumina layer.

Energy of the tunneling electrons, \( E_x \) is the \( x \) component of the energy, and \( \phi(x,V) \) describes the barrier potential. The TRAPSQR barrier potential has the form:

\[
\begin{align*}
\phi(x,V) &= \phi_1 + (\phi_2 - \phi_1)x / d - (x / d + s)V \quad \text{when } x \leq d , \text{ and} \\
\phi(x,V) &= \phi_3 - (x / d + s)V \quad \text{for } d < x \leq s .
\end{align*}
\]

(39)

\( \phi_1, \phi_2 \) and \( d \) represents the barrier heights and thickness respectively associated with the CdS layer (with or without adsorbed 7ETTD), while \( \phi_3 \) and \( s \) are the barrier height and thickness for an assumed present alumina layer. This
type of barrier has been used successfully in different types of systems and known to give reasonable results [60] [64] [65].

Clearly, several possible sets of parameters exist that will satisfy the fit, but only those yielding physically realistic solutions were taken into account. The barrier parameters obtained by fitting the WKB approximation to our experimental G-V data for (i) Al/CdS/Pb and (ii) Al/CdS/7ETTD/Pb junctions, as shown in Figures 24 (a) and (b), are as follows:

(i) Al/CdS/Pb:

\[ \varphi_1 = 3.15 \text{ V}, \varphi_2 = 3.8 \text{ V}, \varphi_3 = 4.59 \text{ V}, d = 0.83 \text{ nm}, s = 0.22 \text{ nm}. \]

(ii) Al/CdS/7ETTD/Pb:

\[ \varphi_1 = 2.65 \text{ V}, \varphi_2 = 2.65 \text{ V}, \varphi_3 = 4.60 \text{ V}, d = 2.1 \text{ nm}, s = 0.42 \text{ nm}. \]

The value obtained for \( \varphi_3 \) (~ 4.6 V) is approximately the same for both types of junction, and is due to the presence of small quantities of native Al-oxide. The barrier parameters above are reasonable, taking into account that the effective barrier parameters in the WKB approximation are average values since the actual area, coverage, and thickness can vary locally. We notice that \( d \) increases by 1.27 nm, when 7ETTD is introduced. The calculated length of the 7ETTD molecule is about 0.6 nm (as determined by Gaussian 98 B3LYP/6-31+g(d,2p) calculations) [63] so, on first inspection, it would appear that we have more than one monolayer of 7ETTD adsorbed on the CdS film. However, it must be emphasized that the increase in thickness for the actual composite tunnel barrier will included contributions due to (1) the presence of surface hydroxyl groups on the CdS film (see section 4.2.3. below), and (2) any thickening of the native
Figure 24. Normalized conductance–voltage dependences (a) Normalized conductance–voltage dependence recorded at 4.2K for an Al/CdS/solvent/Pb tunnel junction (symbols), and WKB approximation fit to the data (solid line). (b) Normalized conductance–voltage dependence recorded at 4.2K for an Al/CdS/7ETTD/Pb tunnel junction (symbols), and WKB approximation fit to the data (solid line).
alumina layer. Both of these are possible when the sample is removed from the vacuum chamber, exposed to ambient conditions, and doped with a solution of 7ETTD. We have allowed for thickening of the alumina layer in our calculations, but the contribution due to surface hydroxyl groups has been neglected. This means that the nominal value of 1.27 nm, obtained for the increase in d, is an upper bound and, therefore, consistent with the presence of approximately one adsorbed monolayer of 7ETTD.

The WKB fits for low bias (0 to ~ 0.2 V) are very good and the results above indicate that the dopant decreases the effective barrier height while increasing its thickness. However, WKB fits for voltages above ~ 0.2 V yield poor fits indicating that mechanisms other than tunneling come into play at higher bias. This is also probably why vibrational modes are attenuated in the IET spectra at higher bias since tunneling no longer accounts for the majority of the charge transport through the junctions at this higher bias. Since the HOMO LUMO gap for 7ETTD is too large to decrease the potential barrier, we propose that surface states-orbital coupling occurs, leading to a significantly increased conductance. One also notices that the G(V,T) plot for Al/CdS/Pb is highly asymmetrical because of the barrier height asymmetry (3.15 V and 3.8 V for \( \varphi_1 \) and \( \varphi_2 \) respectively).

When the molecule is adsorbed on the surface and conducting channels are formed, the barrier becomes more symmetrical, and the corresponding G(V,T) plot is also more symmetrical, since electrons can travel through those channels avoiding tunneling.
4.2.3 IET, IR, Raman and calculated spectra

Figure 25 is a typical IET spectrum obtained from an Al/CdS/7ETTD/Pb sample. (For comparison to conductance-voltage data, note that 1 cm\(^{-1}\) = 8.065 mV, so that the spectral range 0 to 4000 cm\(^{-1}\) corresponds almost exactly to the bias range 0 to 500 mV. This conversion does not account for the \(\sim 8\) cm\(^{-1}\)

![Graph of a typical IET spectrum](image)

Figure 25. Typical IET spectrum obtained from an Al/CdS/7-ETTD/Pb junction.

The downward trend of the background above \(\sim 0.2\) V (\(\sim 1600\) cm\(^{-1}\)) is indirect evidence that tunneling is not a predominant mechanism for conduction at high bias. Usually, similar kinds of backgrounds are observed when Fowler-Nordheim behavior observed, but as discussed above, the barrier is too high for this and the current voltage characteristics indicate that this mechanism is absent. In order to see spectral lines more clearly we subtracted a 4\(^{th}\) order polynomial fit from the spectrum of

...
Figure 25 and the resulting spectrum is presented in Figure 26 together with the corresponding MRAIR spectrum. Figure 27 shows a Raman spectrum of 7ETTD compound crystal structure, on gold and on CdS surface.

Table 2 shows a comparison of MRAIR spectral data for 7ETTD adsorbed on CdS and IR data for a 7ETTD bulk crystalline powder sample. All base peaks match to a large degree. Assignments of the peaks were made based on Gaussian calculations (Gaussian 98 B3LYP/6-31+g(d,2p)) [63] of the vibrational spectrum of the molecule. We now turn to the orientation of 7ETTD on the CdS surface. Based on the MRAIR spectrum, we infer that 7ETTD molecules are adsorbed on CdS via their sulfur crowns. Evidence for this is the $\equiv$C-H stretching mode at 3259 cm$^{-1}$ which is very intense indicating that the molecules are oriented such that their triple bonds are aligned essentially perpendicular to the CdS surface, consistent with MRAIRS selection rules. The $\equiv$C-H peak is not shifted from its normal bulk value and so the $\equiv$C-H group is not expected to interact with the CdS surface. This would be most unlikely in any case because there is no known mechanism for it to do so. Rather, we can be reasonably confident that the sulfur crown at the other end of the molecule bonds to the surface. These observations are in keeping with what one would expect since these compounds have been shown to adsorb via their sulfur crowns on gold [46] and are expected to do the same for other materials. We should mention that identifying direct evidence for vibrational modes associated with the bonding between sulfur atoms in the crown and the CdS surface is difficult with IR spectroscopy because (1) the CdS is amorphous, so there will be a range of
Figure 26. Spectra of CdS layer doped with 7ETTD. (a) MRAIR spectrum of CdS layer doped with 7ETTD, (b) IET spectrum obtained of the Al/CdS/7-ETTD/Pb sample of Figure 23 after subtraction of 4th order polynomial background, (c) calculated spectrum of 7ETTD [63].
expected bond energies, and also (2) they occur at the low end of the IR spectrum where detector sensitivity is very low. However, the MRAIR spectra presented here clearly display strong peaks due to the adsorbed 7ETTD molecules which are in agreement with the model for adsorption via their trithiaadamantine anchors discussed above.

We know of no other work to investigate the adsorption of sulfur containing compounds on amorphous CdS. XPS is a technique that one might consider to investigate this further, but the ability of XPS to detect any sulfur peaks related to molecule-CdS surface interactions is extremely doubtful because a surface-related sulfur peak would be expected to appear as a shoulder on the essentially bulk background sulfur peak from the CdS layer and with an intensity several orders of magnitude weaker. MRAIRS appears to be a far better way to investigate the adsorption mechanisms.
Table 2.

Peak assignments for 7ETTD adsorbed on CdS and for a bulk 7ETTD crystal powder sample [63].

<table>
<thead>
<tr>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignment</th>
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<tr>
<td>on CdS</td>
<td>Bulk</td>
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<tr>
<td>830</td>
<td>829</td>
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<td>920</td>
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<td>3259</td>
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4.3 CdS nanoparticles

The Raman spectrum of the nanoparticles is presented in Figure 28(a).

The spectrum shows asymmetric broadening of CdS peak. In comparison, in the spectrum of CdS film, CdS phonon peak at 302 cm$^{-1}$ is almost completely symmetrical. It is known that the distribution of Raman scattering lines is dependent on particle size and information from this broadening is maybe
analyzed to estimate the CdS nanoparticle size. Assuming that CdS nanoparticles are small spherical semiconductor crystals, one can determine their size based on the Cardona, Trallero-Giner theory. The corresponding frequencies of the scattered light are:

\[ \omega^2 = \omega_{LO}^2 - \beta_L^2 \left( \frac{v_n}{R} \right)^2 \]  

where \( \omega_{LO} = 305 \text{ cm}^{-1} \) is the bulk vibrational mode [65] [66] and 

\[ \beta_L = 1.054 \times 10^2 \text{ m/s} \]  

\( v_n \) is \( n \)-th root of the Bessel function \( j_1 \). \( n \) is the principal quantum number. Figure 29 represents the dependence of vibrational mode energy on nanoparticles radius \( R \). The contribution to the spectrum from different modes \( n=1, 2, \ldots \) can be estimated: [68]
Figure 29. Radial dependence of optical vibration modes for Raman excitation (n is the quantum number)

\[ B_n = 8\pi^3 R_0^3 \left[ \frac{2(1 - \cos \nu_n) - \nu_n \sin \nu_n}{3\nu_n \cos \nu_n - (3 - \nu_n^2) \sin \nu_n} \right]^2 \] (41)

Figure 30(a) shows the result of this deconvolution of the Raman spectrum for our synthesized CdS nanoparticles and scale down of three main contributors (Figure 30(b)) to the spectral line (dots represent actual data, dashed lines are the three deconvoluted harmonics n=1,2,3 and the straight line is the sum of those three harmonics). The lines were chosen to be Lorentzian type with the centers corresponding to the crossing of the vertical line with the functions of frequencies on Figure 30. The contribution of the largest three modes were set according to [67]. The fit was performed using a MATLAB algorithm least square method. Analysis of the Raman fitting parameters gives a value of 42 Å for the estimated CdS nanoparticles radius. Direct measurement of the nanoparticles size by AFM, give a value of 450 Å. Figure 31 represents a typical AFM image of the nanoparticles.
Figure 30. The result of application of the deconvolution of the Raman spectra of CdS nanoparticles. (a) Large range and (b) scale down of three contributors to the spectral line (dots represent actual data from, dashed lines are the three harmonics $n=1,2,3$ and the straight line is the sum of three harmonics)
4.4 AFM and EFM investigation and modification of CdS films

Figure 32 is a typical image of CdS sputtered onto an Al film evaporated onto a glass substrate. The CdS film thickness is 100 nm measured with a quartz thickness monitor. Commercially available imaging software [Scanning Probe Image Processor ~Image Metrology ApS.] was used to characterize the film. A familiar granular structure is observed, similar to most sputtered films, which are formed by nucleation and growth. The grain size is approximately 30–40 nm, and the root-mean-square surface roughness is calculated to be 1.8 nm. A lower root-mean-square surface roughness is being observed for films produced for IETS, since much thinner films are needed for tunneling mechanism to be observed.

The system in the present AFM/EFM study is effectively an electrochemical cell comprised of the AFM tip, a water bridge between the tip and
Figure 32. AFM image of CdS sputtered on Al substrate (a) true non-contact mode (b) phase image. The thickness of CdS film is 100 nm and the thickness of Al is approximately 100 nm

the surface, unsaturated water vapor in vicinity of the tip due to electrostatic attraction of water molecules to the biased tip, and a surface film. The system is shown schematically in Figure 33. The humidity in the system was maintained and controlled by a dynamic filtered air flow method. The patterned nanostructures were imaged and their topography and electric charge distribution at the surface were recorded over a period of several seconds after the ZAM protocol was completed. The results are presented in Figure 34. A comparison of the patterned features with corresponding EFM images from the same location indicates that charge is deposited on the CdS surface, and remains there for 5–
Figure 33. Experimental configuration of the tip/water meniscus/surface system. (a) A nanoscale electrochemical cell. The water monolayer on the dielectric and other surfaces has been omitted for clarity. (b) The humidity is monitored by wet/dry bulbs, and controlled using a dynamic gas filtration system.

10 min before it finally drains via the conductive substrate. However, AFM imaging of the nanostructures 7 days later showed no structural changes. EFM measurements indicated that the sign of the charge at the CdS surface was positive, i.e., opposite to that of the negatively biased AFM tip. It is well known that a weakly biased AFM tip forms a tiny water bridge under 20%–40% ambient humidity [69]. Electric breakdown in water occurs in the presence of an electric field larger than $10^7$ V/m. Electric field between AFM tip and the surface approaches $10^9$–$10^{10}$ Vm$^{-1}$, which is the case for the present 10–20 V biased
Figure 34. Examples of geometric functionalization of the a-CdS surface. (a) 30 nm (8 nm high dots), (b) 50 nm (22–25 nm high dots), (c) 100 nm (10–16 nm high dots), (d) 200 nm (40 nm high dots), and (e) 500 nm (35 nm high dots) films. The tip is retracted from the surface to a distance in the range of 50–250 nm; the tip bias is varied between −20 and −40 V. The height of the features increases from 8 to 40 nm, which appears to correlate with film thickness. EFM data suggest that positive electric charge is deposited on the surface in the darker colored regions as shown and dissipates 5–10 min later. However, all the physically patterned features remain intact for 7 days. (e) Example of silicon surface oxidation using the ZAM protocol (the tip is retracted from 50 to 250 nm and a negative bias of −15 V was applied): the height of the features was less than 3 nm.
AFM tip separated from the surface by a distance of 0.5–2 nm. It has been reported recently [70] that electric breakdown inside the water bridge initiates field-induced water ionization producing free electrons as follows:

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- + e^- \]

From previous work [44], it has been suggested that the abundance of electrons, generated inside the water bridge is responsible for an anomalous electric current of 100–500 A in magnitude observed on the surface of n-type Si, which has similar physical properties to CdS. Studies suggest that electric breakdown in water is common and takes place in a variety of the systems involving high magnitude electric field and dielectric, or in semiconductor substrates, and we anticipate this to be the case in the present CdS work. Because of local structural variations of the tip and CdS surface the large dc electric field due to the biased AFM tip in proximity to the grounded CdS film may exceed \(10^8–10^9\ \text{Vm}^{-1}\). This field is sufficient to break Cd–S bonds and trigger ionized mass transport through the CdS films. However, electrochemical reactions at the CdS/water interface which may also produce Cd ions cannot be ruled out. For example, it has been proposed that photocorrosion of CdS occurs in the presence of dissolved oxygen in aqueous solution [71] [72]. In this photocorrosion process, light is essentially an initiator which generates electron-hole pairs in the CdS films. After a series of reactions involving the CdS film, holes, and oxygen in the aqueous solution, the net result is that \(\text{SO}_4^{2-}\) and \(\text{Cd}^{2+}\) ions are the main photoproducts. In the present work we propose that the large electric field close to the biased AFM tip provides the energy required to create the electron-hole pairs in the initiation step. Then,
once the Cd ions have been created, oxidation mechanisms and/or mass transport of the Cd ions are possible causing deposition of oxide products and/or Cd ions at the CdS surface creating the observed nanostructures. This suggests transport of material vertically from below the nanostructures towards the surface along electric field lines. Clearly, further work is required to determine the exact nature of the mechanisms leading to nanostructure formation. A useful starting point would be the investigation of the following observations in support of a mass transport mechanism: (a) The height of the nanostructures (8–40 nm) patterned on CdS is much greater than that of structures patterned on silicon due to the surface scanning oxidation. ZAM protocol has been used to pattern nanostructures on crystalline Si(110) surfaces and the results indicate that their height does not exceed 3 nm. (b) The height of the structures on CdS appears to correlate with film thickness; we have observed 8 nm structures on a 30 nm films, 22–25 nm on a 50 nm films, 10–16 nm for 100 nm films, 40 nm for 200 nm films, and 35 nm for 500 nm films. Future work to confirm this correlation would support the hypothesis that the material is displaced vertically. (c) The structures on CdS remain the same for a substantial period of time; if the sole mechanism for nanostructure formation were oxidation, the structures would be expected to change over time. This lends further support to our suggestion that a combination of processes is responsible for their formation. In summary, we have developed a patterning technique, ZAM, which creates raised columnar nanostructures of 150 nm wide to 40 nm high on amorphous CdS films. Although sequential in nature, ZAM protocol allows robust geometric surface functionalization. It is anticipated
that ZAM can be implemented for biological applications, precise surface modification, where large area functionalization is not required, and for photovoltaic applications in other semiconductors (possibly organic). Based on the height of the structures and their stability over time, it is suspected that a plausible physical explanation for the formation of these nanostructures is related to a combination of oxidation and ionized mass transport along the lines of very strong nonuniform electric field although further investigations are required to elicit the exact nature of these mechanisms.

Figure 35 presents topographical images illustrating the effect of humidity on surface functionalization for amorphous CdS. For all the samples, AFMEN protocol was applied under variable humidity conditions (Hr was varied from 10 to 60%). Humidity was controlled by in house modification of AFM (Figure 33(b)). The overall similarity of the current-voltage trends for both insulating (PMMA, PS) and semiconductor (CdS) substrates suggests that the water meniscus plays a major role in supplying charge for the process. Generation of electrons in the meniscus is triggered at voltages exceeding a substrate-specific threshold, provided that the relative humidity stays above 20%. As a consequence, the measured output current increases while the input current stays limited. For polymeric films, the current inside the film is carried by electrons under the breakdown regime [32] [41].
Figure 35. Nanostructures patterned in 50-100 nm thick CdS films using AFMEN protocol: (a) $H_r > 50\%$; The electric voltage did not exceed -20 V; The height of the structures varied between 4 and 10 nm, and the width between 150 and 170 nm; (b) $H_r = 25\%$; An array of dots was patterned for the tip bias -18 V; The width of the structures was between 100 and 150 nm, and the height of the structures varied between 5 and 7 nm; (c) $H_r < 17\%$; The width of the patterned dots was 40-50 nm, the height of the dots was less than 5 nm; In all experiments the temperature was maintained around 19 °C [73].
4.5 Adsorption of PANI, PMMA and TES on CdS

To increase the efficiency of hybrid organic photovoltaics, certain device designs incorporate semiconductor nanoparticles (CdS) imbedded in a polymer matrix to increase the effective polymer/semiconductor interface area. To simulate the boundary between conductive polymer matrix materials and CdS nanoparticles, we investigated the adsorption of PANI, PMMA and TES on sputtered CdS films using MRAIRS. The samples were prepared in a way similar to IETS junctions with but omitting the Pb electrode. After spin coating the CdS film with polymer solution, all samples were returned to the vacuum chamber to remove any weakly bound materials. For reference purposes, Figure 36 shows the IET spectrum of PMMA adsorbed on Al. Acid-base interactions take place between the amphoteric alumina surface and carbonyl functional groups of PMMA [74]. The result is ionic bonding between the alumina surface and carboxylate structure. The spectrum shows the presence of symmetric at 1452 cm\(^{-1}\) and asymmetric at 1592 cm\(^{-1}\) deformation modes of carboxylate groups. The C=O peak at 1740 cm\(^{-1}\) is very weak, indicating cleavage of the ester group has occurred. Figure 37 presents the FTIR spectrum of Al/CdS (60A)/ PMMA film. The strongest peak in the spectrum is C=O at 1740 cm\(^{-1}\), which means very little or no reaction between the carbonyl and the CdS surface has taken place. The presence of PMMA on the surface suggests a strong physical adsorption.
Figure 36. IET spectrum of PMMA adsorbed on Al oxide.

Figure 37. FTIR spectrum of Al/CdS (60A)/ PMMA film.
Figure 38 represents FTIR spectrum of CdS doped with PANI. There are no adsorption bands from aniline, and therefore it is safe to conclude that PANI does not adsorb on CdS. The spectrum of CdS doped TES is shown in Figure 39. No characteristics features of TES are present. Its been concluded that TES does not adsorb on CdS.

Figure 38. FTIR spectrum of CdS / PANI film.

Figure 39. FTIR spectrum of CdS / TES film.
Several surface-specific techniques have been deployed to successfully characterize the structure, charge transfer mechanisms, and adsorption mechanisms of amorphous CdS surfaces. The findings are as follows.

5.1 Adsorption of 7ETTD on CdS thin films

IET and MRAIR spectroscopic data indicate that 7ETTD molecules self-assemble and adsorb on ultra-thin CdS films via their adamantane anchors such that they are aligned with their axes essentially perpendicular to the surface. The MRAIRS data, in particular, are more conclusive than IETS and strongly suggest that the molecules are adsorbed via their trithia-adamantane anchors. The adsorbed 7ETTD layer significantly modifies the conductance-voltage behavior of the tunnel junctions under investigation and it is observed that tunneling is no longer the predominant conduction mechanism for junction biases above ~ 0.2 V. At these higher biases a frontier orbital coupling mechanism between HOMO and LUMO levels of the 7ETTD molecules and surface states on the CdS offers a plausible explanation for the observed conductance-voltage behavior. Due to the significant effect on junction behavior it appears that further investigation of this
family of compounds, with particular attention to their applicability in molecular electronics, is justified.

5.2 Adsorption of PANI, PMMA and TES on CdS thin films

PANI and TES do not adsorb on CdS. Those materials can not be used for modification of interfaces to increase performance devices based on CdS. PMMA on other hand physisorbs and offers the possibility for use as a host matrix in organic-inorganic hybrid nanocomposites.

5.3 Surface functionalization of a-CdS films.

A robust patterning technique, z-lift amplitude modulated atomic force microscopy assisted electrostatic nanolithography (ZAM), has been applied for the first time on semiconductor surfaces (CdS). The technique is based on the vertical manipulation of a negatively biased oscillating Atomic Force Microscope (AFM) cantilever. We have shown ZAM to be capable of functionalizing the surface morphology of amorphous CdS, just as a variety of polymers at room temperature. The technique delivers proof of concept for fabrication of photovoltaic devices with increased surface area, possibly leading to greater carrier generation per linear surface area.

An analysis of electric current-voltage behavior at different humidity levels suggests that electrons supplied by water ionization during the patterning stage are responsible for the observed sustainable electric current between the AFM tip – sample junction. The process of nanostructure formation is associated with
combination of ionization of the surface, electrochemical oxidation and possibly mass ion transport. The similarity of the surface patterning in CdS and polymer films with significantly different physical and chemical processes suggests that observed characteristics of nanostructures formations are primarily determined by the water meniscus.

5.4 CdS nanoparticles
The size of nanoparticles synthesized at UA has been determined from analysis of Raman spectroscopic data. It is concluded that IETS could be used to investigate the charge transport phenomena within nanoparticles by recording the spectra and conductance-voltage behavior obtained from MIM junctions where the insulating layers composed of nanoparticles films or nanoparticles imbedded in a host matrix, e.g. PMMA.


APPENDIX

Cardona, Trallero-Giner developed a unified method valid for any spherical nanostructure to describe Frohlich-type electron-phonon interactions [75] [76] [77]. Similar approach and results were obtained by Vasilevskiy, Rolo and Gomez in 1997 for arrays of nano-crystals [68]. The model considers polar optical phonon dispersion up to quadratic terms in the wave vector and the coupling between the mechanical vibration displacement $\vec{u} = \vec{u}(\vec{r})e^{-i\omega t}$ and the electrostatic potential $\Phi$. For a single quantum dot of radius $R$, equation of motion takes form:

$$
\rho(r)\left[\omega^2 - \omega_{TO}^2(r)\right]\vec{u} = \nabla\left[\rho(r)\beta_L^2(r)\nabla \cdot \vec{u}\right] - \nabla \times \left[\rho(r)\beta_T^2(r)\nabla \times \vec{u}\right] + \alpha(r)\nabla \Phi \tag{42}
$$

where $\rho$ is the reduced mass density, $\omega_{TO}$ - the TO bulk phonon frequency, $\beta_L$ and $\beta_T$ are the phenomenological parameters estimated from the experimental phonon dispersion relations and

$$
\alpha = \sqrt{\frac{(\varepsilon_0 - \varepsilon_\infty) \rho \omega_{TO}^2}{4\pi}} \tag{43}
$$

Where $\varepsilon_0$ and $\varepsilon_\infty$ are the static and high frequency dielectric constants.

Maxwell’s equation for electric field $\vec{E} = -\nabla \Phi$ gives:

$$
\nabla \cdot \left(\varepsilon_\infty \nabla \Phi\right) = 4\pi \nabla \cdot (\alpha \vec{u}) \tag{44}
$$
The potential $\Phi$ is the solution of Poisson equation, where $-\nabla \cdot (\alpha \vec{u})$ is a charge density. Therefore, one can present the potential $\Phi$ to be a result of the polarization field [76]:

$$\vec{P} = \alpha \vec{u} - \frac{\varepsilon_e}{4\pi} \nabla \Phi$$

Equations (32) and (34) are coupled second-order partial differential equations for $\vec{u}$ and $\Phi$. To save continuity for them at the surface of quantum dot with radius $R$:

$$\vec{u}\big|_{r=R^-} = \vec{u}\big|_{r=R^+} \quad \text{and} \quad \Phi\big|_{r=R^-} = \Phi\big|_{r=R^+}$$

The full solution of coupled second-order partial differential equations can be found with an auxiliary scalar function $\Lambda$ and a vector function $\vec{\Gamma}$, that satisfy:

$$\vec{u} \cdot \nabla = \Lambda$$

and

$$\vec{u} \times \nabla = \vec{\Gamma}$$

Equation (32) can be transformed by applying curl operator and using that

$$\nabla \times \nabla \times \vec{u} = \nabla (\nabla \cdot \vec{u}) - \nabla^2 \vec{u} :$$

$$(\nabla^2 + Q^2)\vec{\Gamma} = 0$$

where $Q^2 = \frac{\omega_{TO}^2 - \omega^2}{\beta_T^2}$.

Applying the divergence operator to equation (32):

$$(\nabla^2 + q^2)\Lambda = 0$$

where $q^2 = \frac{\omega_{LO}^2 - \omega^2}{\beta_L^2}$.

$\omega_{LO}$ and $\omega_{TO}$ are connected with Lydane-Sachs-Teller relationship:
\[ \omega_{LO}^2 = \frac{\varepsilon_0 \omega_{TO}^2}{\varepsilon_\infty} \]  \hspace{1cm} (50)

Substituting (47) into (44):

\[ \vec{\nabla}^2 \Phi = \frac{4\pi \alpha}{\varepsilon_\infty} \Lambda \]  \hspace{1cm} (51)

The general solution for the potential:

\[ \Phi = \Phi_H - \frac{4\pi \alpha}{\varepsilon_\infty q^2} \Lambda \]  \hspace{1cm} (52)

where \( \Phi_H \) is the solution of Laplace’s equation.

After substituting (52) and (47) into (44), the general equation for any type of nanostructure:

\[ \vec{u} = -\vec{\nabla} \left[ \frac{\alpha}{\rho \beta^2 Q^2} \Phi_H + \frac{\Lambda}{q^2} \right] + \frac{1}{Q^2} \vec{\nabla} \times \vec{\Gamma} \]  \hspace{1cm} (53)

For each particular case, one can apply the boundary condition to solve for \( \Phi_H \) Laplace’s equation and solve Helmholtz’s equation for \( \Lambda \). For spherical boundary conditions:

\[ \Phi_H = Y_{lm}(\theta, \varphi) \begin{cases} C_l r^l, & r < R \\ C_{l-1} r^{l-1}, & r > R \end{cases} \]  \hspace{1cm} (54)

\[ \Lambda = Y_{lm}(\theta, \varphi) \begin{cases} A_l j_l(qr), & r < R \\ A_{l} h_{l}^{(1)}(qr), & r > R \end{cases} \]  \hspace{1cm} (55)

where \( Y_{lm}(\theta, \varphi) \) with \( m = -l, \ldots, l \) and \( l = 0, 1, \ldots \) are the spherical harmonics, \( j_l \) and \( h_{l}^{(1)} \) the Bessel and Hankel spherical functions, and \( C_l, A_l \) (\( i = 1, 2 \)) constants to be determined.
By Raman scattering the spherical (l=0) and spheroidal quadrupolar modes (l=2) can be observed. The spherical modes are excited for parallel polarization of the incident and scattered light. The most important contribution corresponds to l=0. The eigenvalue equation is obtain from setting the displacement to zero:

$$\ddot{u}_{l=0} = A j_l \left( \frac{r}{R} \right) \vec{e}_r,$$

(45)

where $\nu_n$ is n-th root of the Bessel function $j_1$.

The vibrational shifts can be found from (38) and are the longitudinal type:

$$\omega^2 = \omega_{LO}^2 - \beta_l^2 \left( \frac{\nu_n}{R} \right)^2$$

The contribution to the spectra from different modes n=0, 1, 2, ... can be estimated and was done by Vasilevskiy, Rolo and Gomez in 1997 [68]:

$$B_n = 8\pi R_0^3 \left[ \frac{2(1 - \cos \nu_n) - \nu_n \sin \nu_n}{3\nu_n \cos \nu_n - (3 - \nu_n^2) \sin \nu_n} \right]^2$$

(56)

If an interaction takes place within many nanocrystals, there is another contribution to Raman scattering due to a collective vibrational-electromagnetic excitation of the Frohlich type, but its contribution is less significant.