# THIN FILM SUBSURFACE ENVIRONMENTS; ADVANCED X-RAY SPECTROSCOPIES AND A NOVEL BAYESIAN INFERENCE MODELING ALGORITHM

by

Jonathan R. Church

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering

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#### ABSTRACT

New condensed matter metrologies are being used to probe ever smaller length scales. In support of the diverse field of materials research synchrotron based spectroscopies provide sub-micron spatial resolutions and a breadth of photon wavelengths for scientific studies. For electronic materials the thinnest layers in a complementary metal-oxide-semiconductor (CMOS) device have been reduced to just a few nanometers. This raises concerns for layer uniformity, complete surface coverage, and interfacial quality. Deposition processes like chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been shown to deposit the needed high-quality films for the requisite thicknesses. However, new materials beget new chemistries and, unfortunately, unwanted side-reactions and by-products. CVD/ALD tools and chemical precursors provided by our collaborators at Air Liquide utilized these new chemistries and films were deposited for which novel spectroscopic characterization methods were used. The second portion of the thesis focuses on fading and decomposing paint pigments in iconic artworks. Efforts have been directed towards understanding the micro-environments causing degradation.

Hard X-ray photoelectron spectroscopy (HAXPES) and variable kinetic energy X-ray photoelectron spectroscopy (VKE-XPS) are advanced XPS techniques capable of elucidating both chemical environments and electronic band structures in sub-surface regions of electronic materials. HAXPES has been used to study the electronic band structure in a typical CMOS structure; it will be shown that unexpected band alignments are associated with the presence of electronic charges near a buried interface. Additionally, a computational modeling algorithm, Bayes-Sim, was developed to reconstruct compositional depth profiles (CDP) using VKE-XPS data sets; a subset algorithm also reconstructs CDP from angle-resolved XPS data. Reconstructed CDP produced by Bayes-Sim were most strongly correlated to the real chemical distributions in our CMOS.

Chemical speciation and degradation mechanisms in paint pigment materials from iconic artwork has been investigated using high energy X-rays by the techniques as X-ray absorption near-edge spectroscopy (XANES) and X-ray fluorescence (XRF). Unique features in X-ray absorption spectra using XANES help identify the chemical species present in the paint sample by comparing similar spectral features from known reference standards. By carefully choosing X-ray energies that excite a subset of the present chemical species the distribution of constituents can be determined. This work furthers the understanding of supposed photo-oxidation degradation mechanisms and potential preservation efforts to maintain the painting integrity for cadmium yellows used in Henri Matisse's *Le Bonheur de vivre* and arsenic sulfides from an 18th century still life painting from Adriaen Coorte.

# Chapter 1 INTRODUCTION

#### 1.1 Moore's Law and Technology Nodes

Since the emergence of integrated circuits their geometric properties and key performance markers have been driven by an industry wide operating principle: Moore's Law. Moore's law is not a mathematically proven formula, nor is it a strict set of rules implemented by a governing body. The most common definition can be traced back to 1975 when Gordon E. Moore projected the "complexity" of devices to double every two years [1], this was later modified to represent a doubling in component density on a chip every 18 months [2].

With the explosion of component chip density a convenient measure of progress was the minimum distance between components/structures in a complementary metaloxide-semiconductor (CMOS) which colloquially became known as device "technology nodes". Aided by Moore's law, mapping technology node trends synchronized industry partners and competitors alike, driving the global market to smaller and faster electronic devices. To understand the rapid pace of technological development, consider the minimum feature size in semiconductors. In 1960 the minimum feature size was 50  $\mu$ m, but by the mid-1990's had decreased two-hundred times to 250 nm.(see Fig. 1.1). Now in 2015 the limit is being pushed below 20 nm, an over two-thousand fold decrease since 1960.

Unfortunately the physical lengths between regions are approaching fundamental limits. The transistor gate length,  $L_g$  (see Fig. 1.2), is often used as the smallest repeat unit in CMOS and is a good example; it is the conduit through which electrical current travels and decreasing its length means faster switching times. On the other



Figure 1.1: Historical minimum feature sizes reported by the International Technology Roadmap for Semiconductors (ITRS) from 1995-present. In the mid-1990's the physical gate length (red line) outpaced the scaling of the M1 half-pitch measured between lines in the first metal layer (blue cross hatch). Source: Gargini ITRS ©2013 IEEE

hand decreased gate length also increases short channel effects (SCE) caused by overlap of source and drain depletion layers. In part the solution was to revolutionize the geometry of the transistor with 3D technology. Non-planar technology was introduced commercially at the 22 nm node with Intel's tri-gate [3].

The distinguishing feature of Intel's Tri-Gate is a raised channel region, seen in Fig. 1.3. By wrapping the raised "fin" in a gate dielectric provides better electrical control over the conducting channel.

In the context of material design for integrated circuits, CMOS, and electronic devices this work will discuss how modern processing reliably deposits layers of material



Figure 1.2: Simplified schematic of planar transistor technology showing the three main regions in a device: source, gate, and drain.  $L_g$  is the physical length of the gate.

at nanometer length scales. Much of the progress made in these technologies has been in the refinement of chemical vapor deposition (CVD) methods and development of atomic layer deposition (ALD) as a viable growth technique. With new chemistries CVD and ALD are extensible to a large portion of elements in the periodic table from which follows the need for comprehensive material characterization.



Figure 1.3: Planar FET (left) and FinFET Tri-gate (right) technology. Planar technologies use stacked gate geometry with a gate dielectric (green) deposited directly over the channel's surface, seen in yellow. In the tri-gate a gate dielectric covers the top and side walls of a raised channel region. Source: Intel Corporation

Unwanted contaminants and side-reactions are inherent to the development of

most new reaction chemistries. These can be characterized using a combination of elemental distribution analyses and high resolution microscopy studies. This work will utilize the capabilities of X-ray photoemission spectroscopic tools to study both chemical and electrical environments. The XPS studies will be complemented by scanning electron microscopy and transmission electron microscopy studies to gather visual information concerning morphological properties.

Each new generation of electronic devices and the materials supporting them will need ever more refined metrological studies. This dissertation encompasses many of the tried and true methods used to bring electronics into the new millennium and also considers potential advancements seen at state-of-the-art synchrotron facilities and how statistical modeling can be utilized with ever more computational power producing larger and larger data sets.

#### **1.2** Interfaces and Regions of Interest

Smaller features means active regions in a device can exchange electrical signals more quickly. Tighter geometry also increases the density of devices per wafer thereby decreasing system fabrication costs. From a design perspective this also means previously distant, isolated interfaces are now in closer proximity. Bulk like behavior breaks down near surfaces and therefore interaction between multiple interfaces introduces phenomena that could previously be ignored. Also, because of the material scarcity in each layer even low concentrations of defects and inhomogeneities may now have pronounced effects.

A significant amount of material research has focused on the gate region of the transistor. As mentioned in the previous section the shortest distance between repeat units in devices is the physical gate length. To add to the processing demands the gate oxide happens to also be the thinnest region in the whole device; at the 65 nm technology node the physical gate thickness was 1.2 nm[4]. It had already been reported in 1999 by Muller *et al.* that a fundamental roadblock [5] would be reached trying to push the thickness below 1.2 nm. Transition between the silicon substrate and the  $SiO_2$  dielectric introduces an interfacial region with a minimum roughness of 0.7 nm and with oxide growth methods would not be able to achieve smaller than 1.2 nm roughness. Thus, after the 65 nm node new materials were introduced in the gate so that performance could still be increased without having to further thin this layer.

#### **1.2.1** Replacement Gate Dielectrics

With support from fundamental research the industry quickly adapted high- $\kappa$  technology in the gate dielectric. High- $\kappa$  refers to the dielectric constant or relative permittivity value, the term "high" is used to highlight the fact that it is a value greater than  $\kappa=3.9$  [6] - the value for the (former) industry standard SiO<sub>2</sub>. Rapid growth of microelectronics was supported in no small part by the characteristics of SiO<sub>2</sub>; it is an excellent insulator with a large band gap, can be patterned to very small feature sizes, and is easily grown using thermal oxidation of silicon. The problem is, when the thickness of SiO<sub>2</sub> approaches one nanometer quantum effects begin to play a role, and tunneling induces leakage currents. To understand the need for higher  $\kappa$  values let's consider the gate dielectric to be a parallel plate capacitor in a linear circuit whose capacitance value is:

$$C = \frac{\kappa \epsilon_0 A}{t} \tag{1.1}$$

where  $\epsilon_0$  is the permittivity of free space, A is the capacitor's surface area, and t is the physical thickness of the capacitor. Increasing A, of course, runs counter to Moore's scaling trends so device engineers had to consider increasing relative permittivity values. Disregarding any processing demands the simplest solution would be to completely replace SiO<sub>2</sub>. From this singular design goal oxides possess the highest  $\kappa$  values, for example a titanate like SrTiO<sub>3</sub> has a  $\kappa$  near 2000 [7]. Thermodynamic stability between contacted materials, however, is a primary concern that could lead to interdiffusion or unwanted chemical reactions. Hubbard and Schlom effectively eliminated a large portion of the periodic table's binary oxides by only considering a stable interface between the silicon substrate and the oxide [8]. Their method calculated the Gibb's free energy for a reaction involving a binary oxide and silicon, and therefore the thermodynamic stability (see Eqns. 1.2 and 1.3).

$$\operatorname{Si} + MO_x \to M + \operatorname{SiO}_2$$
 (1.2)

$$\operatorname{Si} + M\operatorname{O}_x \to M\operatorname{Si}_z + \operatorname{SiO}_2$$
 (1.3)

where  $MO_x$  is the binary oxide containing the binary oxide's candidate metal M. If the Gibb's energy for the three component system ( $\Delta G > 0$ ) was lowered for temperatures between 0-1000 K this led to elimination of that material from possible candidates. This method can also be extended to ternary oxides like SrTiO<sub>3</sub>. They were able to show that TiO<sub>2</sub> is not thermodynamically stable with SiO<sub>2</sub> and therefore eliminated. Choices for potentially thermodynamically stable binary oxides were narrowed down to alkaline earth oxides, rare earth oxides, Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, UO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>.

The next round of material selection was then made with a fair amount of confidence that the high- $\kappa$  layer would be chemically stable on silicon. Robertson took up the challenge by not only providing relative permittivity values but also crucial energy band calculations for the strongest candidates[7, 9]. Without proper band offsets the gate dielectric would not be an effective insulator. A standard rule of thumb is that the valence band and conduction band of the gate dielectric must possess band offsets of 1 eV or greater from silicon for proper operation. It follows then, that wide-band gap and high- $\kappa$  materials will be favored over others. By plotting the relationship between the relative permittivity and band gap Robertson showed a tendency for the  $\kappa$  values to follow an inverse curve with band gap seen in Fig. 1.4 [10]; simply choosing the highest  $\kappa$  material was no longer a practical choice for gate dielectrics.



**Figure 1.4:** Plot of relative permittivity values,  $\kappa$ , vs. band gap. Reprinted with permission from J. Robertson, J. Vac. Sci. Technol B, 18, 1785 2005, Copyright 2005

After Hubbard, Schlom, and Robertson's work the key properties of replacement gate dielectrics had been identified. A good figure of Merit for practical application in devices was to plot the leakage current density as a function of the dielectric's effective oxide thickness (EOT). The EOT was, and is, used to relate any new gate dielectric to SiO<sub>2</sub>; it is the thickness of SiO<sub>2</sub> needed to achieve the same capacitance  $C_{SiO_2}$  for any high- $\kappa$  layer of capacitance  $C_{High-\kappa}$ . If we recall Eq. 1.1 we can start with the relations:

$$C_{\rm SiO_2} = C_{\rm High-\kappa} \tag{1.4}$$

$$\frac{\kappa_{\mathrm{SiO}_2}\epsilon_0 A}{EOT} = \frac{\kappa_{High-\kappa}\epsilon_0 A}{t_{High-\kappa}} \tag{1.5}$$

where  $\kappa_{SiO_2}$  is 3.9 for SiO<sub>2</sub>,  $\kappa_{\text{High}-\kappa}$  is the relative permittivity for the replacement dielectric, and  $t_{\text{High}-\kappa}$  is the physical thickness of the replacement dielectric. Rearranging the equation provides:

$$EOT = \frac{3.9 \times t_{\text{High}-\kappa}}{\kappa_{\text{High}-\kappa}} \tag{1.6}$$

It was quickly realized that lanthanides possess the lowest leakage current for a given EOT, yet their reactivity with water made processing difficult and  $HfO_2$  was chosen as the first replacement gate dielectric.

In Fig. 1.5 a cross-sectional transmission electron microscope (TEM) images show the transition from an all SiO<sub>2</sub> gate oxide to a hafnium-based high- $\kappa$  dielectric [11]. Notice that poly-silicon was replaced with a metal layer as well. Looking to the future device engineers will begin implementing high mobility channel regions located under the gate dielectric for better performance. Similarly, the introduction of new channel materials will rely on large scale research efforts.



Figure 1.5: Cross-sectional TEM image for transistor technology at 65 nm and 45 nm nodes. Gate region circled in red. Gate dielectric replacement also encouraged the replacement of Poly-Si as the contact material. Source: Gargini ITRS ©2013 IEEE

A gate metal avoids depletion effects that are present in poly-Si, eliminates the need for a high temperature dopant activation step, and improves the electrical conductivity [12]. There are two approaches to the introduction of a gate metal: midgap and band-edge. The mid-gap approach deploys a gate metal with a work function,  $\Phi_{\rm m}$  located in the middle of the silicon's band gap, see Fig. 1.6. Because silicon's band gap is 1.1 eV the transistor threshold voltage V<sub>th</sub> will be around 0.5 eV for both nMOS and pMOS devices and tends to be too large for high performance devices. Using band-edge metals eliminates this problem by using two separate metals, one with a work function approaching silicon's conduction band ( $\Phi_{\rm m,nMOS}$ ) and the other with a work function near silicon's valence band ( $\Phi_{\rm m,pMOS}$ ). Threshold voltages for band edge nMOS and pMOS devices, V<sub>th,nMOS</sub> and V<sub>th,pMOS</sub> respectively, are significantly lower than mid-gap metals. Costs and processing complexity are the major disadvantages for the band-edge approach. To date the debate about the gate metal is an ongoing area of research.



**Figure 1.6:** Two approaches to gate metal design: mid-gap approach (left) and the band-edge (right). nMOS gate metal possesses a work function near silicon's conduction band edge (green) while the pMOS metal's work function is near silicon's valence bad edge (red).

### 1.3 Characterization Approach

Comprehensive elemental distribution analyses are needed to aid in taking advantage of beneficial material properties. There are numerous techniques to study elemental compositions in solid thin films: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), electron dispersive X-ray spectroscopy (EDS or EDX), and electron energy loss spectroscopy (EELS) are the most common techniques. XPS is uniquely capable of simultaneously providing electrical environment information in addition to elemental and chemical information and will therefore be the primary technique used.

### 1.3.1 X-ray Photoelectron Spectroscopy



Figure 1.7: XPS experimental set up. High energy electrons from a heated filament strike an anode generating X-rays. X-rays are focused onto a sample where electrons are emitted from and collected by an electron analyzer that calculates the electrons kinetic energy based on their trajectory. The read out shows the number of detected electron signals as a function of energy.

In an XPS system (Fig. 1.7 [13]) the X-rays are generated by high energy electrons striking an anode target which most often is either made of magnesium or aluminum. Magnesium and aluminum emit X-rays at well known energies. X-rays are then focused to a sample where electrons are emitted based on the photoelectric effect, whereby incident radiation can eject electrons from material if the energy of the incident photon is sufficient to overcome the material's energy barrier to emission, or its work function  $\Phi$ . The maximum kinetic energy of the ejected electrons follows:

$$KE = h\nu - BE - \phi_D \tag{1.7}$$

where  $\nu$  is the photon's frequency, BE is the electron's binding energy, and  $\phi_D$  is the detector's work function.

By measuring the energy of photo-generated electrons one can determine the elemental constituents in a given sample because chemical species possess characteristic binding energies that are usually distinctly resolvable. Multiple chemical states can be identified either because its characteristic peak is shifted far from the "pure" elemental peak or the peak may be broadened and/or non-symmetric. Similarly, the electrical environment in a thin film can have a strong enough effect to shift electrons kinetic energy in a measureable way which will also show up as peak shifts or peak broadening.

XPS is especially surface sensitive, though, which makes studying buried layers a challenge and when multiple nano-layer films are stacked on top of each other quantifying the depth resolution becomes an important factor. Though the X-rays can penetrate microns of material it is the limited distance which electrons can travel through media that limits the probing depth. Once a photoemitted electron is generated it will undergo inelastic scattering events, decreasing its kinetic energy and decreasing the probability of detection. For the most common XPS systems the effective probing distance is only around 2-5 nm. To study buried layers of material XPS systems are usually outfitted with an ion-sputtering system. The sputtering system will contain an inert gas, often argon, which is ionized and then accelerated towards the sample. High energy argon ions will then physically remove layers of material. Among the drawbacks of this approach is disturbing the unaffected environments present in the sample but less obvious is the preferential sputtering away of some atoms over others. For long enough sputter times, the preferential removal of elements could lead to misinterpretation of XPS data for compositional calculations. A key example of this was seen in work done by Baker *et al.* seen in Fig. 1.8[14].



Figure 1.8:  $MoS_2$  sputtered depth profile (left) for reference powder of 1:2 stoichiometry for molybdenum and sulfur respectively and Mo 3*d* core level spectra before and after sputtering (right).

Using a reference powder of  $MoS_2$  XPS spectra were collected at different intervals to study the potential preferential sputtering effects. Simply calculating the relative atomic concentration percentage between molybdenum and sulfur as a function of sputter times exhibits a fairly large effect; sulfur concentration drops rapidly from the reference value of 66%. Fig 1.8 shows the XPS spectrum for Mo 3*d* of the native surface (top-right). There are two sharp peaks seen with the main one located at 229.25 eV and a full-width half maximum of 1.02 eV. As sulfur leaves the material some molybdenum atoms will be left to compensate by bonding to either other sulfur atoms or molybdenum atoms. Evidence for more oxidation states of molybdenum atoms can be seen in the XPS spectra for a post-sputtered sample. The spectrum shows a shift in the main peak to lower binding energy by almost 1 eV to 228.3 eV. The post-sputtered Mo 3d peak also broadens by .23 eV to 1.25 eV, this is suggestive of a relative increase in secondary peaks under the main peak.

In chapters five and six statistical methods have been applied to non-destructive X-ray photoelectron spectroscopy (XPS) techniques to extract elemental compositions as a function of depth. I discuss a new search algorithm, Bayes-Sim, that randomly samples a probability event space composed of candidate depth profiles. The Bayes-Sim algorithm applies Bayes' theorem to establish a "goodness" value of each depth profile and the simulated annealing schedule as a construct to administer conditional tests. Bayes-Sim can be applied to both variable-kinetic energy XPS (VKE-XPS) and angle-resolved XPS (AR-XPS) data and in this work a practical application of the algorithm is demonstrated with simulations of VKE-XPS data for C 1s, Al 2p, O 1s, and Si 1s core levels in a 23 nm Al<sub>2</sub>O<sub>3</sub> film deposited on silicon. Favorable simulations tend to closely match the results from a depth profile collected by an ion-sputtering process.

#### 1.3.2 Microscopy

No matter how dependable or detailed other analyses are visualization of sample materials will continue to be a crucial analytical tool. Imaging can be used to gather topographical information, degree of crystallinity, and morphological properties like conformality and uniformity. Two principle methods to image nano-layers are: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM scans a highly focused beam of electrons on a sample and collects the emitted secondary electrons to contrast different topographical features. Most often sample preparation and data collection is more straightforward than with TEM and for this reason is often used to quickly generate images. Though TEM requires manipulation of smaller and more fragile samples it is absolutely fundamental in the research of electronic devices because its resolution capabilities are unmatched by any other method.

### 1.4 Interfaces and Band Measurements

XPS can also be used to monitor energy band alignments in semiconductors. It has been shown that determining the valence-band edge from core level spectra is possible using XPS as long as the precision is better than  $\pm 0.1$  eV [15]. Charge density along interfaces or surfaces often differ from the values found in bulk portions of material and according to Poisson's equation the charge distribution establishes a spatially varying electrostatic potential which bends all of the bands or energy levels by  $qV_{BB}$  (seen near the interface in Fig. 1.9).



Figure 1.9: Energy band diagram showing the interface of a semiconductor (Material A) and another material (Material B). In the bulk portion of Material A energy bands are flat until approaching the interface with Material B. Amount of band bending  $qV_{BB}$  and depletion width  $x_d$  is determined by the charge density at the interface. The band gap  $E_g$  is the difference in energy between Material A's conduction and valence bands and remains a constant at all depths.

Though not trivial, careful adjustment of experimental parameters makes use of XPS' surface sensitivity to study band bending at different depths in a film; different thickness samples or the geometric location of the chemical species as a depth reference can be used for energy band analysis. High X-ray energies provide the added benefit of extended probing distances. Known as hard X-ray photoelectron spectroscopy, XPS at a synchrotron beam line can improve the probing distance by an order of magnitude over standard methods and because it is non-destructive this approach is ideal for studying the energy band alignments in MOS stacks.

In chapter four, HAXPES analyses were carried out on metal-oxide-semiconductor (MOS) samples consisting of Si, thick and thin  $Al_2O_3$ , and a Ti metal cap. Using Si 1s and C 1s core levels for an energy reference, the Al 1s and Si 1s spectra were analyzed to reveal information about the location and roles of charges throughout the MOS layers. With different oxide thicknesses (2 nm and 23 nm) the depth sensitivity of HAXPES is exploited to probe different regions in the MOS structure. Post Ti deposition results indicated unexpected band alignment values between the thin and thick films, which are explained by the behavior of mobile charge within the  $Al_2O_3$  layer.

#### 1.5 Science in Art

Somewhat unexpectedly the science of semiconductors can be translated to studying artwork. Fundamentally, studying microstructure and chemical compositions can be adapted to any material system and that was where the approach for "Science in Art" began.

Evidence of the degradation of paint layers is becoming more and more of an issue for many iconic artworks. Some paint pigments tend to decompose over time leading to discoloration and flaking. The questions faced by curators and conservationists is first: "what is the degradation mechanism" and second: "what, if anything, can be done to protect the work"? Materials scientists are now being deployed to answer the former, which will be reflected in chapter seven.

#### 1.5.1 Synchrotron Micro-analysis

One of the biggest challenges in this field is the collection of useful samples for analysis. Simply accessing the sample, whether because it is on display in a museum or the region of the painting degrading is in an especially high profile spot on the canvas, can be an arduous process. For this reason samples are often on the order of tens to hundreds of microns. Therefore extremely high spatial resolution techniques are deployed.

Synchrotrons provide a highly focused beam of radiation and, given the rarity of the sample, also provides the added benefit of being non-destructive. X-ray absorption near edge spectroscopy (XANES) is technique which produces a fingerprint signal associated with different chemical compounds.  $\mu$ XANES is the technique adapted for synchrotron beam lines and provides the capability to generate chemical maps for sub-micron spot sizes.

### 1.6 Objective

The motivation behind this work is to develop new schemes that study nanoenvironments and predominant larger scale behavior in solid material systems. The surface science community has been fortunate to see a growth in techniques adapted to synchrotron beam lines and as a result have explored micro-environments with increasingly better resolution.

Chapter two will cover the processing demands for generating uniform nanolayers of material. Chapter three introduces the merits of synchrotron beam lines as well as some of their limitations. Chapter four deploys a high resolution synchrotron XPS technique HAXPES to study subsurface electrical environments. The next chapter, chapter five, develops a statistical approach to generate simulated compositional depth profiles. Chapter 6 will discuss the development of a new software tool J-FAB adapted to variable XPS experiments and can automatically compute chapter five's simulations. Finally, chapter seven covers the author's contributions to recent microanalysis of iconic artwork using XANES.
## Chapter 2

# NANOMETER LAYER MATERIAL PROCESSING

Rapid growth in electronic technologies and down scaling trends have been aided by the development of more sophisticated material processes. The entire fabrication facility must be able to support each refined process, and, given the sophistication of each step it is best to have the entire industry follow the same schedule; with that in mind we can understand the importance of technology nodes.



Semiconductor Fabrication

Figure 2.1: Semiconductor wafer process flow.

Compatibility between each processing step is of crucial importance. Each process in semiconductor fabrication seen in Fig. 2.1can be thought of as its own discipline with a substantial amount of literature being published each year. Often processing can span many weeks for fabrication of an IC device, and given the hundreds of processing steps technologies must consider the effects each step has on the history and future of that IC device. For the current work I will focus on the "adding" steps. These are steps that add atoms to a wafer either by deposition, ion implantation, diffusion, or oxidation/nitridation.

This chapter will discuss deposition methods this work used for the analyses in chapters 4-6. Physical vapor deposition will be introduced briefly as it was used to deposit a thin metal capping layer of titanium. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) make up a significant portion of the material source as well as scientific investigations and will therefore will include a much more rigorous discussion. Both CVD and ALD experiments were made possible by collaborations with our industrial partners at Air Liquide at their Delaware facility (Delaware Research and Technology Center) and their Japanese facility (Air Liquide Laboratories).

## 2.1 Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) is another method to deposit thin films. Unlike CVD or ALD the source material for PVD processes can use pure elemental targets. The targets can be vaporized by heating them to high enough temperatures to induce evaporation or can be bombarded with high energy ions whereby sputtered target atoms impinge on the desired surfaces. Often, PVD is used for deposition of metallic materials or metallic alloys.

## 2.2 Chemical Vapor Deposition (CVD)

CVD gives process engineers flexible designs for mass transport and the extensibility of vapor phase chemical reactions. Changing process conditions makes the deposition of many types of materials for different applications possible. For example, low temperature CVD is deployed for depositing insulating amorphous material for the dielectric region in CMOS. Alternatively, increasing the temperature enables the deposition of pure, epitaxial silicon. The general sequence follows:

- Prepare surface of substrates for desired chemical reactions
- Stabilize the CVD system for operating set points (i.e. pressure, temperature, flow rates, deposition time, etc.)
- Introduce chemical reactant precursors to the deposition chamber
- Chemical reaction byproducts produce desired material and deposit on the substrate while un-wanted byproducts flow out of the chamber
- Process continues until desired thickness or coverage is achieved

There are three main types of CVD systems: atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD), and plasma-enhanced CVD (PECVD).

APCVD using a conveyor belt to move substrate wafers underneath a flow of precursor gases which deposit on the wafer. APCVD tends to grow layers of film the quickest and can therefore be used to deposit thicker layers of material.

For more precise layer-to-layer control LPCVD and PECVD are deployed. A typical LPCVD/PECVD reactor can be seen in Fig. 2.2 and usually operates at pressures around 1-10 Torr. Pressure is controlled by use of a vacuum system and the rate of flow for the gases entering the system. Reduced pressures in the reaction chamber tend to favor surface limited chemical reactions. As a result of surface dependencies the wafer temperature is the primary variable to control reaction kinetics; parameters like growth rate, surface coverage, and byproducts are all carefully studied as a function of temperature.

Upper limits on temperature set points are limited, however. Increased temperatures can cause phase changes, induce chemical species migration throughout material stacks, or cause precursor decomposition. Also, recall that any previously fabricated layers must be stable for forthcoming process temperatures. PECVD, on the other hand, avoids downfalls seen in LPCVD processes. PECVD yields high quality conformal films and overcomes kinetic barriers without increasing temperatures by using a plasma source to ionize reactants. The ionized atoms strike the substrate, increasing



Figure 2.2: CVD system outfitted with an RF coil for inducing a plasma

the surface mobility of other surface species and improving coverage. An additional benefit is that LPCVD equipment can easily be modified with a plasma generator and operate in either LPCVD or PECVD mode.

## 2.2.1 CVD Precursors

Some of the most exciting work for CVD of electronic materials is done in the design of new chemical precursors for both dielectric materials and metals. There is an extensive and growing list of precursors available for CVD[16, 17, 18]. The most common precursor ligand groups and their properties are listed in Table 2.1. Notice that a significant amount of attention is focused on the metallic-carbon bond. Unique bonding properties of the carbon atom allow chemists to tailor organo-metallic precursors for different situations. Specifically, the covalency of carbon bonding makes organo-metallic precursors relatively stable in ambient conditions but reactive enough

to catalyze efficient ligand cleavage. Still, matching processing conditions while maintaining the integrity of the precursor's desired properties can be a challenge; eliminating carbon contaminants and unwanted byproducts still needs significant attention.

Ligand group	Advantages	Disadvantages	Molecular structure
Halides	Volatile, cheap, stable, reactive	Corrosive byproducts, contaminants, solid phase	M-X (X=F,Cl,Br,I)
Alkyls	Highly reactive, high growth rates, inert byproducts	Low decomposition temperatures, carbon contaminants	M-R (R=simple alkyl)
Alkoxides	M-O bond in molecule for binary oxide dep.	Only oxides deposited, difficulty cleaving oxygen reactive byproducts	M-OR (R=other organic species)
<i>β</i> -diketonates	Broad elemental compatibility, moderate decomposition temperature	No nitrides, bulky ligand, carbon contaminants	$M-O_2-R_1-R_2$ ( $R_1,R_2=$ organic species)
Cyclopentadienyls	Highly reactive, relatively large growth rates, temperatures, stable byproducts	Limited knowledge low decomposition carbon contaminants	M-Cp
Alkylamides	Broad elemental compatibility, highly reactive	Low decomposition temperatures, impurities	M-ONR (R=other organic species)

Table 2.1: Common classes of CVD precursors to deposit metal atoms (M) which are organized by different ligand groups. Attempts to optimize each precursor have led to specialization of different precursor molecules for increasingly narrow applications. Additionally, CVD is being used for a diverse set of material systems with stricter processing demands. Fortunately, a general set of design rules are used to help inorganic chemists and process engineers design robust CVD molecules. Those rules are:

- Volatile readily vaporizes within process temperatures
- Suitable temperature window possesses a large enough temperature range between volatilization and decomposition
- Ambient stability stable in storage at room temperature
- Clean pyrolysis limited contamination when the precursor thermally decomposes
- Cost effective cost-efficient synthesis routes with high yields
- Safe reasonable safety measures should be adequate

#### 2.3 Atomic Layer Deposition (ALD)

An increasingly popular variant of CVD is atomic layer deposition (ALD). ALD uses a very similar experimental set-up to the one seen in Fig. 2.2 except reactants are pulsed separately into the reaction chamber. The ideal ALD process is also self-limiting, meaning once the substrate's surface is uniformly covered all chemical reactions cease, even if there is surplus un-reacted chemical precursor present. ALD growths continue sequentially, depositing one monolayer of material at a time, see Fig. 2.3 for a typical ALD cycle. Therefore, thicknesses can be precisely and simply controlled by decreasing or increasing the number of cycles. In the following study I will introduce development of zirconium precursors for depositing  $ZrO_2$  films by ALD.

# 2.3.1 ALD Precursors

Interest in ALD has increased since the early 1990's, and is partly in response to the need for extremely thin and conformal layers in microelectronics. ALD is especially beneficial for the gate oxide discussed in section 1.2.1. Conveniently, process engineers



**Figure 2.3:** A typical four step ALD cycle with two reactant pulse/purge steps. The first reactant, a metal containing precursor, is pulsed onto the surface and purged after self-saturation. The second reactant cleaves the metal's ligands and is purged from the reaction chamber leaving only the metal atoms on the surface.

and chemists could use many of the same precursors used in CVD like those seen in Table 2.1 with the additional constraint of self-limiting surface reactions.

The first extensive case study for ALD surface chemistry was performed by Puurunen [19] in 2005. She chose an "ideal" ALD reaction using trimethyl aluminum (TMA) and water as reactants. In Puurunen's review there were two key elements to ALD growths. First, chemisorption must be the predominant adsorption method. Strong interactions between the solid surface and reactants lead to chemisorption where the chemical bonds form only with the surface leading to a single monolayer of adsorbed species. Physisorption, on the other hand, may include non-adsorbate-to-surface interactions and lead to multilayers. Second, irreversible saturating adsorption is necessary and relies upon the first condition to be met. Physisorption always leads to desorption from the surface (reversible) whereas chemisorption can be either reversible or irreversible. The saturation condition means the surface has been exposed to reactants for a long enough time to enable complete surface coverage.

#### 2.3.1.1 Chemisorption Mechanisms

There are three chemisorption mechanisms that lead to self-saturation of a reactant molecule  $ML_n$  on a surface site || - a to form || - M:

- 1. Ligand exchange Both the metal atom M and ligand(s) L bond to a surface species as aL which are then volatilized. Multiple ligand exchange reactions can continue for different ligands and other surface species but surface to metal bonding, || M, does not increase.
- 2. Dissociation  $ML_n$  is split onto reactive sites on the surface. Ligands L may bond to other surface bound metal atoms to form  $||-ML_{n+1}|$  but metal deposition nor ligand surface bonds increase post-dissociation.
- 3. Association  $ML_n$  chemisorbs on a surface site but does not release ligands and forms  $|| ML_n$ .

## 2.3.1.2 Saturation

Two factors limiting self-saturation are steric forces from precursor ligands and the number of reactive sites. The former is caused by bulky ligands shielding active surface sites from other free precursor molecules. The latter is dependent on both temperature and surface chemistry.

#### 2.3.1.3 ALD Case Study: Zirconium Dioxide Precursors

 $ZrO_2$  was one of the strongest candidates to replace SiO<sub>2</sub>. It is thermally stable on silicon and possesses a high permittivity value relative to SiO<sub>2</sub>. Additionally, there was a wealth of literature being rapidly generated on ALD precursors for  $ZrO_2$  [20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49]. Unfortunately, the precursor studies used mostly halide containing molecules which generated corrosive byproducts and a significant amount of halide contamination within the film. A major advancement came in 2001 when the first reported result of cyclopentadienyl zirconium (IV)(dichloride)

 $(ZrCp_2Cl_2)$  and bis(cyclopentadienyl)dimethyl zirconium(IV) ( $ZrCp_2Me_2$ ) were able to match growth rates only seen previously with  $ZrCl_4$  while reducing process temperatures to 300 °C, decreasing chlorine contamination, and increasing crystallinity. In 2002 new alkylamide precursors were able to push the deposition temperatures even lower to 275 °C [51]. The zirconium alkylamide precursor tetrakis- (ethylmethylamido) $zirconium(IV) Zr(NMeEt)_4$  possessed the characteristic self-limiting reactions for ALD as well as low surface roughness and impurities. Known as TEMAZ it became the industry standard for  $ZrO_2$  deposition. Eventually, new research began to focus on achieving the same quality layers at increased temperatures without the impurities or corrosive byproducts seen with halide containing precursors. It was discovered that higher temperatures tend to favor the tetragonal  $ZrO_2$  phase which possessed a higher permittivity value. Efforts were then made to improve the thermal stability by replacing zirconium-nitrogen bond(s) in TEMAZ with a cyclopental ligand, and it was eventually shown that decomposition could be increased beyond 300  $^{\circ}C$  [52, 53]. The following experiment will investigate the possibility to improve thermal stability of zirconium precursors even more.

#### 2.3.1.4 Experimental

In order to investigate thermal stability dependencies on the ligands in organometallic precursors for ALD multiple  $\text{ZrO}_2$  films were deposited in a custom built cross-flow type ALD reactor on p-Si(100) (10-20 $\Omega$  cm) substrates. Prior to deposition substrates were subjected to a 1% HF dip for 60 seconds, dried, and immediately introduced into the ALD reactor. The zirconium precursor was composed of cyclopentadienyl and alkoxide ligands with a formula  $\text{Zr}(\text{Cp})_x(\text{OR})_{4-x}$  where x is a number between 1 and 3 and R is an alkyl group. Ozone was used as an oxygen source. Variable angle ellipsometry was performed at the center of the ALD deposited wafer to determine thickness values. Substrates were heated between 225-375 °C for 30 minutes for thermal decomposition tests, afterwards thickness was measured. Surface saturation was determined by varying the ALD cycle times for both the precursor and oxidant pulse and purge cycles and then calculating the growth per cycle (GPC).

## 2.3.1.5 Results and Discussion

Thermal decomposition is a result of the precursor's chemical bonds breaking as a result of elevated temperatures before reaching the substrates surface. No oxidants or other reactants are introduced into the chamber at this step. Evidence of thermal decomposition can be seen by a sharp increase in carbon contamination and thickness as a result of unwanted physisorption processes. Thermal decomposition results for our zirconium precursor can be seen in Fig. 2.4. Significant decomposition does not appear until 375 °C, providing evidence that the precursor is stable enough to try at temperatures greater than 300 °C



Figure 2.4: 30 minute decomposition test for zirconium precursor

After passing thermal decomposition tests the precursor's viability for ALD sequencing can be tested. For surface saturation the precursor and ozone will be pulsed into the reaction chamber at separate times. Pulse cycles need to last long enough to completely cover the surface, very long pulse times should not deposit more material for ALD reactions if the precursor is self-limiting. Purge times need to be long enough to evacuate all byproducts and gases from the chamber before the next pulse sequence.



Figure 2.5: Pulse (left) and Purge (right) ALD steps for organo-metallic precursor at 275 °C.



Figure 2.6: Pulse (left) and Purge (right) ALD steps for ozone at 275 °C.

Deposition results for each pulse and purge sequence, or saturation curves, can be seen in Figs. 2.5 & 2.6. Evidence for characteristic ALD precursor saturation can be seen in each of the curves. First, the deposition GPC agrees well with the thickness of monolayers of  $ZrO_2$ , about 1 Å and the precursor pulse curve appears to flatten out for pulse times greater than 10 seconds. Additionally, the ozone pulse time exhibits saturation behavior beyond 5 seconds. A reasonable ALD sequence for this precursor in this system would be 10-20-5-10, with the precursor pulse/purge first and oxidant pulse/purge second.

## 2.3.1.6 Conclusion

ALD experiments were performed for a novel zirconium precursor of the formula  $\operatorname{Zr}(\operatorname{Cp})_x(\operatorname{OR})_{4-x}$ . There is evidence supporting thermal stability exceeding 300 °C, better than most commercial zirconium precursors. There is also characteristic ALD self-limiting behavior seen in the saturation curves.

## 2.4 Final Remarks

More sophisticated chemistries and experimental designs have aided in the progress of the semiconductor industry towards smaller and smaller feature sizes. The ability to tailor chemical precursors for CVD and ALD processes makes them a likely area of specialization for thin film deposition in the future. The approaches used in this chapter can serve as an outline for complementing those processes.

#### Chapter 3

# DEVELOPMENT OF ADVANCED XPS METHODS

X-ray photoelectron spectroscopy (XPS) was introduced in section 1.3.1. It is a powerful characterization technique that provides a wealth of information about the elemental constituents, chemical species, and electrical environments. Traditionally XPS is sensitive to within a few nanometers of a sample's surface and therefore was used to study near surface environments. Even so, there is valuable depth information that can be extracted from careful analysis of the XPS spectra. In this chapter I will discuss variants of standard XPS that help elucidate depth information and improve upon previously limited probing distances.

First, let us consider the photoemission process and how the electron signal intensity varies as a function of depth. The attenuated XPS signal I that originates from a depth z from the sample's surface will decrease exponentially from inelastic scattering according to Beer's Law:

$$I = I(z)exp\left[\frac{-z}{\lambda\sin\theta}\right]$$
(3.1)

where I(z) is the XPS signal originating at a depth z,  $\lambda$  is the electron's inelastic mean free path, and  $\theta$  is the electron's take-off angle relative to the sample's surface.

XPS electron intensities are attenuated by the amount of material the electron has to travel through as well as material properties effecting inelastic mean free paths (IMFP) within a medium. IMFP's will be discussed more in detail later in this chapter. Let us first focus our attention on the take-off angle relative to the sample surface. If we imagine two photoemission processes as in Fig. 3.1 increasing the take-off angle from  $\theta_1$  to  $\theta_2$  shortens the electron's horizontal path length through the film, thereby decreasing inelastic collisions and increasing the detected XPS intensity from depth z, I(z). Alternatively, more normal take-off angles sample deeper into the specimen.



Figure 3.1: Photoemission process using two different electron take-off angles,  $\theta_1$  and  $\theta_2$ . Detected XPS data  $I_1$  will be more surface sensitive compared to XPS data  $I_2$ . Original signal intensity I(z) is attenuated as electrons are inelastically scattered through the film. The relationship between the original intensity I(z) and detected intensity  $I_1$  or  $I_2$  is described by Beer's law, Eq. 3.1.

## 3.1 Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS)

AR-XPS is a variant of XPS with the additional capability to adjust the photoelectron's take-off angle; as the take-off angle relative to the sample's surface varies, so is the likelihood of detecting more deeply buried electrons. The variable angle depth sensitivity therefore can provide composition information as a function of depth by collecting spectra at each angle and identifying angle-to-angle changes or shifts.

#### 3.1.1 Experimental

Al<sub>2</sub>O<sub>3</sub> films were deposited on 100 mm p-type (10-20  $\Omega$  cm) Si(100) substrates. Al<sub>2</sub>O<sub>3</sub> was deposited by atomic layer deposition (ALD) using trimethyl aluminum (TMA) and H<sub>2</sub>O at 300 °C in a Picosun showerhead ALD system. The deposited Al<sub>2</sub>O<sub>3</sub> thin film was 2 nm as determined by variable-angle ellipsometry. The samples were subjected to a thermal treatment of annealing (400 °C, 20 min) and firing (760 °C, 3 s). The firing step was similar to the one used for photovoltaics described elsewhere [54]. Experiments performed on a PHI 5600 series XPS system with an excitation source that generated Al-K $\alpha$  X-rays at 1486.6 eV and were monochromatic. The XPS system pressure was  $2 \times 10^{-9}$  Torr. Si 2p XPS spectra were collected at three different sample surface-to-detector angles, 15°, 45°, 75° for exactly the same collection times.

## 3.1.2 Results and Discussion

The normalized spectra from AR-XPS data can be seen in Fig 3.2. The peak located around 99.0 eV is assigned to the elemental silicon Si  $2p_{3/2}$  and the peak at 102.8 eV is assigned to a sub-oxide silica species.



**Figure 3.2:** Si 2p spectrum for three different angles:  $15^{\circ}$ ,  $45^{\circ}$ ,  $75^{\circ}$ .

There is a significant increase in the sub-oxide peak relative to the elemental silicon peak with angle. This would seem to suggest that a sub-oxide exists on the silicon substrate as larger collection angles denote larger probing depths,. The cause of the sub-oxide layer can be explained by the high temperature processing steps. Recall that the samples were subjected to 450 °C and 750 °C during annealing and firing, previous work using similar thermal treatment established that the Al<sub>2</sub>O<sub>3</sub> system is

prone to an interfacial growth of sub-stoichiometric silica [55]. As the sample surfaceto-detector angle increases it is probing more substrate like silicon, thereby increasing the elemental silicon peak intensity relative to the interfacial oxide.

Unfortunately, detection limits restrict the maximum probe depths to around 3 nm for standard X-ray sources. Attenuation of the electron signal in Eq. 3.1 depends on both the take off angle and IMFP. Calculations by Tanuma, Powell, and Penn put IMFP values for some common elemental electron orbitals like the carbon 1s, silicon 2p, and gold 4f at 1.9 nm, 2.9, nm, and 1.7 nm, respectively [56]. Clearly, pushing XPS probing depths also means increasing IMFPs.

#### 3.2 Development of a Universal IMFP Equation

The inelastic mean free path (IMFP) for an electron is the average distance electron's travel through a medium before losing energy through inelastic collisions. Due to its importance for quantitative surface analysis there has been significant theoretical and experimental work in the last half-century to build a universal equation from first principles that is valid for all elemental and molecular solids. Theoretically, calculations for IMFPs began to emerge for only a few free-electron metals like aluminum in the early 1970's but were hard to verify due to experimental problems [57]. To improve upon the limited application of IMFP calculations scientists looked to the dielectric function, which describes the "stopping" power of a material for moving charged particles. Theoretically, Tung directly calculated IMFP values for free-electron like materials using Lindhard's statistical approximation of the dielectric function [58, 59]. Empirically, Powell used optically derived dielectric values to approximate IMFPs for well known materials [60]. Penn combined Powell's empirical approach and Tung's theoretical calculations, and ultimately derived a formula which could be applied to more materials than ever before [61].

The next hurdle for a universal equation was being able to quantitatively predict the dependence of the electron's path on the medium through which it is traveling as well as its kinetic energy using only material parameters. Powell recognized with his optical data that electrons, when traveling at high enough speeds, exhibited behavior consistent with a theory developed in 1930 by Bethe [62, 63]. The Bethe equation is the cross-section per atom/molecule for inelastic electron scattering at an electron energy E and takes the form [64]:

$$\sigma = \frac{4\pi a_0^2}{E/R} M_{tot}^2 \ln\left[\frac{4c_{tot}E}{R}\right]$$
(3.2)

where R is the Rydberg energy (13.606 eV),  $a_0$  is the Bohr radius (52.9 pm) and  $M_{tot}^2$  is the square of the dipole matrix element for all inelastic scattering processes. The term  $c_{tot}$  is referred to as a "Bethe" parameter and is dependent on the complex dielectric value's dependence on momentum transfer [55]. The Bethe equation is expected to be valid when the electron energy is high enough relative to the scattering energy loss.

It is useful to analyze the relationship between  $\sigma E$  and  $\ln(E)$  in Eq. 3.2 by carrying out multiple experiments at different energies. Plotting this relationship on a special plot, called a Fano plot, Powell showed that the Bethe equation adequately described the energy dependence of cross-sections for the relevant energy range for XPS studies [64].

The cross-section can take on the form  $\sigma = (n\lambda)^{-1}$  where  $\lambda$  is the electron IMFP and  $n = N_a \rho / A$  where  $N_a$  is Avogadro's number,  $\rho$  is the bulk density and A is the atomic/molecular weight. Upon validation of the Bethe equation IMFPs can be related to material parameters and electron energy after rewriting Eq. 3.2:

$$\lambda = \frac{EA}{28.8\rho M_{tot}^2} \ln \left[\gamma E\right]^{-1} \text{\AA}$$
(3.3)

where  $\gamma = 4c_{tot}/R$ . It turns out that the major contribution to the dipole term in Eqs. 3.2 and 3.3,  $M_{tot}$ , scales with the number valence electrons per atom  $N_v$ , and their oscillator strength  $R/\Delta E_a$  where  $\Delta E_a$  is the oscillator energy, or energy transfer in a scattering event. A general formula for IMFPs could now be written with the form [62]:

$$\lambda = \frac{E}{E_p^2 \beta} \ln \left[ \gamma E \right]^{-1} \text{\AA}$$
(3.4)

where  $E_p = 28.8 (N_v \rho/A)^{1/2}$  is the free-electron plasmon energy and  $\beta = 1/(2.12\Delta E_a)$ . Eq. 3.4 is known as TPP-1. Values for  $\gamma$  and  $\beta$  were fitted using optical data and a least-squares approach. The root mean square (RMS) uncertainty with TPP-1 was 12% for energies between 200-2000 eV.

## 3.2.1 TPP-2M IMFP Equation

The ability to calculate IMFPs given only simple material properties density, valence electrons, and atomic weight, made TPP-1 a robust experimental tool for surface analyses. It was discovered, however, below 200 eV the TPP-1 began to show significant departures from optically tabulated values. TPP-2 was developed in response to such limitations, and takes the form [65]:

$$\lambda = \frac{E}{E_p^2 [\beta \ln(\gamma E) - (C/E) - (D/E^2)]} \text{ Å}$$
(3.5)

where:

$$\beta^* = -0.0216 + 0.944 / (E_p^2 + E_g^2)^{1/2} + 7.39 \times 10^{-4} \rho$$
(3.6a)

$$\gamma = 0.191 \rho^{-1/2} \tag{3.6b}$$

$$C = 1.97 - 0.91U \tag{3.6c}$$

$$D = 53.4 - 20.8U \tag{3.6d}$$

$$U = N_v \rho / M \tag{3.6e}$$

\* = Modified to Eq. 3.7

where  $E_g$  is the band-gap energy for non-conductors, M is the atomic molecular weight, both C and D are fitting parameters which depend on U which is depends on previously defined terms. TPP-2 still only requires material properties that can be easily recovered. TPP-2's modifications improved upon TPP-1 in two quantitative ways: the RMS uncertainty over the range 200-2000 eV was lowered to 3% and second, TPP-2 could calculate IMFPs for the lower energy range between 50-200 eV to give an overall average RMS of 13%.

Final modification of Tanuma, Powell, and Penn's IMFP equation came in 1993 with TPP-2M [66]. Outliers for IMFP values calculated using TPP-2 were discovered to be from high-density or low-density regimes. Low-density organics showed a 40% deviation from expected values. Density values strongly influence the  $\beta$  term in TPP-2 and was therefore the only modified parameter. With optical data from 14 different organic compounds Eq. 3.6a was modified to:

$$\beta = -0.10 + 0.944 / (E_p^2 + E_g^2)^{1/2} + 0.069 \rho^{0.1}$$
(3.7)

The result was an improvement in IMFP accuracy for organic compounds from an RMS of 40% to 8.5% and was still accurate for the non-organics. It was shown later that TPP-2M could fit data for much higher energies than previously expected; to date the TPP-2M is valid for 41 elements between 50 eV and 30 keV [56].

#### 3.3 Hard X-ray Photoelectron Spectroscopy (HAXPES)

Synchrotron beamlines increase the capabilities for many areas of scientific research. Using a circular particle accelerator as a light source, beamlines can select desired wavelengths of electromagnetic radiation and focus it to an end station where greater spatial resolutions, increased brilliance, and a large range of energies can be applied to scientific analyses. These characteristics aid in the study of previously unheralded scientific realms and a great deal of new information can be obtained. This dissertation work has applied the unique capabilities of synchrotron beamlines to the advanced XPS technique known as hard X-ray photoelectron spectroscopy or HAX-PES.

HAXPES provides three major advantages over standard XPS. First, the energy range means HAXPES can probe further into samples than standard XPS. Recall Eq. 3.1, increasing the IMFP of electrons through a material increases the likelihood of detection of buried electrons. Then, following the relationship between the electron kinetic energy and IMFP (Eq. 3.5) using a larger energy excitation source leads to larger IMFP and ultimately larger probing depths. Second, increased X-ray energies excite more core levels in atomic orbitals. Consider, for example, a standard aluminum X-ray source which emits X-rays at 1486.6 eV. The largest electron binding energy that can be excited is limited to a  $BE = 1486.6 \text{ eV} - \phi_D$  (Eq. 1.3.1). A maximum binding energy of almost 1.5 keV eliminates key higher binding energy core levels (like the Si 1s = 1839.5 eV or Al 1s = 1562 eV) used in this dissertation. More elemental peaks to study provides alternative peaks where peak overlaps are a concern or as a secondary confirmation for primary core level peak intensities/locations. Third, circular particle accelerators generate a greater brilliance compared to standard X-ray anodes, providing upwards of  $10^{12}$  photons/second [67]. This means even weak XPS signals can be sufficiently detected.

## 3.3.1 NIST X24A Beamline at BNL NSLS

The beamline used in this work was made available by our collaborators at the National Institute of Standards and Technology (NIST), who operate beamline number X24A at Brookhaven National Laboratory's National Synchrotron Light Source (BNL NSLS). The beamline was outfitted with parallel constant-offset double-flat-crystal Golovchenko-Cowan monochromator to select X-rays in the energy range 2.1-5 keV, design can be seen in Fig. 3.3. Wavelength,  $\lambda$ , selection was carried out by use of Bragg's law of defraction,  $2dsin(\theta) = n\lambda$ , where d is the lattice spacing in the crystal and  $\theta$  represents the angle between the sample surface and incident X-rays. A nickel-coated graphite mirror was used for beam collimation and a nickel-coated quartz mirror

was used for final focusing.



Figure 3.3: Parallel constant-offset double-flat crystal Golovchenko-Cowan monochromator design. The two crystals are mechanically connected and rotated together to select desired wavelengths. Bragg angle of incidence  $\theta$  is also shown.

It is important to point out that under irradiation from the beamline the crystal monochromators experience significant thermal fluctuations. The X24A beamline has been outfitted with a water cooling system to dissipate thermal loads, as well as a feedback stabilization system to offset further irregularities. For high-resolution experiments however, a final energy reference should be established and there are multiple methods for accomplishing that task. The energy reference introduced in this work in the following is, to the author's knowledge, a novel approach.

## 3.3.2 Co-spectral Energy Referencing

This section will discuss in detail how precise energy calibrations were established for experiments on NIST's X24A beamline. Over the course of an experiment, the X-ray flux coming from the synchrotron decays, leading to a change in the thermal load on the monochromator and a corresponding drift in the photon energy. The nature of the crystal monochromator makes achieving energy resolutions better than 0.1 eV a challenge, and therefore an in-situ energy reference was introduced.

#### 3.3.2.1 Initial Monochromator Calibration

Before experimentation began initial crystal orientation was established using a clean silver foil. Ag  $3d_{5/2}$  is silver's most intense XPS peak and is located at a binding energy of 368.3 eV, and it follows that the X-ray energy should be:

$$h\nu = 368.3 \text{ eV} + KE$$
 (3.8)

where KE is the kinetic energy of the strongest XPS peak.

Silver was chosen because it has a large sensitivity to X-rays, does not form a significantly oxidized surface, and there are no peaks from common atmospheric contaminants (oxygen, carbon) in the energy range that may be mistaken for the Ag  $3d_{5/2}$ .

## 3.3.2.2 In-situ Energy Reference

Three different methods for a consistent energy reference were considered:

- 1. Ag  $3d_{5/2}$  The silver identified before and after data collection, however this does not provide an in-situ energy check as desired
- 2. Simultaneous reference/sample data collection The X-ray beam can be positioned over two separate samples. the drawback of this approach is a decreased intensity signal for the sample of interest as well as edge effects not present in the bulk portion of the sample material
- 3. Co-spectral method Use multiple well known core levels present in the sample as complementary energy references. This simultaneously allows one to determine the X-ray energy on the sample without compromising the quality of the data.

#### 3.3.2.3 Co-spectral Reference Methodology

To demonstrate the co-spectral energy reference method I will apply it to a MOS system composed of an  $Al_2O_3$  layer and a titanium cap. The  $Al_2O_3$  layer was deposited on a silicon substrate under the same conditions as in section 3.1.1, and the titanium metal was deposited by evaporation. Two different  $Al_2O_3$  samples were deposited, one was 2 nm thick while the other was 23 nm thick. Titanium metal was then deposited on each of the thin and thick samples. The four samples have been identified in Fig. 3.4. The thin un-capped and capped samples will be referred to as 2-Al and 2-Ti respectively; and the thick un-capped and capped samples will be referred to as 23-Al and 23-Ti respectively.



Figure 3.4: Thin un-capped (a), thin capped (b), thick un-capped (c), and the thick capped (d), MOS samples are shown. Gray particles on the surface denote the adventitious carbon layer.

For this work there are core levels from: titanium, oxygen, aluminum, carbon, and silicon to consider. Titanium is only present on the samples that were metallized and thus cannot be used as a consistent reference. Oxygen can be present at the surface as a contaminant, in the  $Al_2O_3$ , or in the interfacial  $SiO_x$  region leading to multiple chemical state binding energies. Aluminum will be affected by electric fields present. The other two to consider are carbon and silicon core levels.

# C 1s Core Level

This atomic orbital was used because carbon is deposited adventitiously upon exposure to atmospheric conditions. This is useful for referencing a wealth of different materials for HAXPES, however the type of carbon species on the surface may drastically change for high surface area oxides like alumina. They show a propensity to adsorb large amounts of oxidized carbon species and without peak fitting this will lead to an underestimate of up to 0.5 eV reference binding energy [68]. Without a detailed analysis of the adventitious carbon, peak fitting the C 1s core level is highly suspect due to the overlap of other carbon species. Alternatively, for studies that compare films of similar compositions adventitious carbon is a good reference and this is exploited in this work

## Si 1s Core Level

Silicon's 1*s* atomic orbital provides an excellent reference given the probe depth is deep enough sample to substrate. Caution should be exercised, however, as the greatest amount of band bending occurs near the silicon surface where charges accumulate. If the probing distance is not large enough a reliable reference value cannot be obtained. The probe distance was at least 28 nm as we detect a faint Si 1s signal for the 23-Ti sample. Knowing this, and, that our substrate is lightly doped to  $10^{15}$  cm<sup>-3</sup> band bending effects should be negligible.

#### **Complementary Approach**

Beginning with the Si 1s binding energy (BE), references [69] and [70] set the BE to 1839.5 eV. All core level spectra for samples 2-Al and 2-Ti are shifted relative to their Si 1s offsets. The binding energies for each of those samples' C 1s BE was then recorded as:

- BE-Al = 286.15 eV
- BE-Ti = 285.7 eV

Finally, BE-Al and BE-Ti are used to reference the thicker 23-Al and 23-Ti samples, respectively.

The C 1s HAXPES data for all four samples can be seen in Fig. 3.5. To summarize, initial energy calibration was performed with a clean silver foil only. Then, HAXPES spectra for the thinnest samples (2-Al and 2-Ti) were collected. Shifts in those samples' Si 1s peak binding energies relative to a value of 1839.5 eV were recorded and then unilaterally applied to all spectra. Because  $Al_2O_3$  is a high-polarity, highsurface area material and the carbon may not be electrically isolated from the sample [68, 71] it is expected that the C 1s binding energies will be different for samples 2-Al and 2-Ti. Those carbon core level binding energies were recorded as BE-Al and BE-Ti, respectively, and will be used to energy reference the thick samples 23-Al and 23-Ti.

# 3.4 Variable Kinetic Energy Hard X-ray Photoelectron Spectroscopy (VKE-XPS)

Straightforward X-ray energy adjustment with the crystal monochromators used for HAXPES measurements has enabled the development of variable kinetic energy hard X-ray photoelectron spectroscopy or VKE-XPS. VKE-XPS studies are a collection of individual HAXPES experiments at different X-ray beam energies to reveal systematic sample dependencies. To understand how VKE-XPS will be used in the coming chapters recall Beer's law from Eq. 3.1. AR-XPS was identified as a method to exploit Beer's law to elucidate information about buried environments by varying the



Figure 3.5: C 1s HAXPES spectra for samples 2-Al, 2-Ti, 23-Al, and 23-Ti. The co-spectral energy reference sets identical binding energies for similar surfaces. 23-Al is shifted to match 2-Al's C 1s binding energy at 286.15 eV, whereas 23-Ti is shifted to 2-Ti C 1s binding energy at 285.7 eV.

electron take-off angle in section 3.1. VKE-XPS varies IMFP ( $\lambda$ ) values, as opposed to take-off angles, to extract depth information from HAXPES spectra.

VKE-XPS intensity calculations will be introduced in this section, and energyto-energy dependencies on relative atomic concentrations will be revealed. Scientific applications for manipulation of VKE-XPS data will be discussed in the chapters five and six.

## 3.4.1 Sensitivity Factors

An important consideration to be made when calculating relative atomic concentrations with XPS, AR-XPS, or VKE-XPS data is each atomic orbital's relative sensitivity factor (RSF). Established sensitivity factors for XPS data are widely available for common Al and Mg X-ray sources [72]. However, for synchrotron radiation sources there are such a large number of experimental configurations that a reference of RSFs would be impractical in use. In the most general case, a relative intensity ratio, X, for species A, is calculated with RSFs using the following formula:

$$X_A = \frac{I_A/R_A}{\sum_j I_j/R_j} \tag{3.9}$$

where I is the XPS intensity and R is the RSF, and the denominator is summed over all species, j.

According to [73] a proper sensitivity factor calculation will account for the species' atomic density n, photoionization cross-section  $\sigma$ , inelastic mean-free path (IMFP)  $\lambda$ , angular anisotropy  $\Theta$ , the X-ray's flux f, probe area A, and the detector's transmission function T. The full sensitivity factor for a species A equation reads:

$$R_A = n_A \sigma_A \lambda_A \Theta f A T \tag{3.10}$$

Neglecting the experimental factors  $\Theta$ , f, A, and T, the material parameters required for proper calculation of Eq. 3.10 can often be approximated or looked up with an acceptable level of accuracy. Material density  $n_A$  is often approximated using bulk stoichiometry of a known material reference, or can be experimentally determined by analytical techniques like X-ray reflectivity [74]. IMFPs are calculated using Eq. 3.5, and requires inputs for the materials band gap (for non-metals), number of valence electrons, material density, and atomic molecular weight. The third material property, or more precisely atomic orbital property, is the photoionization cross-section  $\sigma$ . Photoionization cross-sections for all atomic subshells have been collected for atoms with  $1 \leq Z \leq 100$  for electron energies between 100-5000 eV in data tables [75, 76]. Upon calculation of the electron's kinetic energy with Eq. 1.3.1, most of the relevant materials' cross-sections can be estimated.

#### 3.4.2 Experimental

ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> films were deposited on 100 mm p-type (10-20  $\Omega$  cm) Si(100) substrates by ALD using ozone as an oxidant at 300 °C in a homemade ALD reactor, see Fig. 3.6. Deposited ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> thin films were 6.2 nm and 4.3 nm thick, respectively, as determined by variable-angle ellipsometry. VKE-XPS data was collected at the NIST X24A beamline at BNL NSLS using six monochromatic, collimated X-rays at energies: 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 keV. Relative atomic concentrations for core levels Zr 3d, Nb 3d, O 1s, and Si 2p were obtained by using peak fitting software with Shirley background subtraction. Sensitivity factors were approximated by available bulk stoichiometric data.



**Figure 3.6:** Three layer material stack composed of ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> ALD deposited layers on a silicon substrate

#### 3.4.3 Results and Discussion

Relative atomic concentration (A.C.) distributions as a function of beam energy can be seen in Fig. 3.7 and parameters for RSF calculations are shown in Table 3.1. Notice that the lowest beam energy (2500 eV) data point closely matches the stoichiometric  $\text{ZrO}_2$  for a Zr:O ratio of 1:2, evidence that at 2500 eV the  $\text{ZrO}_2$  region is the major contribution to electron signals. Additionally, a decrease in the Zr 3*d* relative atomic concentrations with beam energy is evident, while both Nb 3*d* and Si 2*p* increase with energy. The oxygen core level, on the other hand, stays mostly constant. These results are consistent with the assumption that larger probing distances are achieved with higher binding energies; it follows that the relative intensity signal from the buried atoms (i.e. niobium and silicon) increase with beam energy. Oxygen stays mostly constant as it is abundantly present for both oxide films. The results also suggest that the substrate can be probed with a 10.5 nm thick overlayer deposition, something that is not possible with lab based XPS systems.



**Figure 3.7:** VKE-XPS results showing relative atomic concentration vs. beam energy for the elemental species: Nb 3*d*, O 1*s*, Zr 3*d*, and Si 2*p*.

Elemental Species	Beam Energy (eV)	Photoionization Cross-section	IMFP (nm)	Atomic Density $(mol/cm^3)$
$\operatorname{Zr} 3d$	2500	9.537	4.41	0.138
	3000	4.134	5.19	0.138
	3500	2.844	5.94	0.138
	4000	1.553	6.67	0.138
	4500	1.127	7.74	0.138
	5000	0.701	8.09	0.138
Nb $3d$	2500	10.913	4.41	0.061
	3000	4.80	5.19	0.061
	3500	3.318	5.94	0.061
	4000	1.829	6.67	0.061
	4500	1.331	7.74	0.061
	5000	0.833	8.09	0.061
$O \ 1s^*$	2500	5.597	3.91	0.042
	3000	3.107	4.7	0.042
	3500	2.300	5.46	0.042
	4000	1.493	6.2	0.042
	4500	1.158	6.92	0.042
	5000	0.824	7.63	0.042
Si 2p	2500	2.080	4.58	0.083
2	3000	0.881	5.35	0.083
	3500	0.606	6.10	0.083
	4000	0.332	6.83	0.083
	4500	0.242	7.54	0.083
	5000	0.152	8.24	0.083

**Table 3.1:** Material parameters used in the VKE-XPS sensitivity factor calculation.\* = Oxygen atomic densities are a linear combination of the oxygen molefractions in  $ZrO_2$  and  $Nb_2O_5$  weighted by the thicknesses of 6.2 nm and4.3 nm, respectively.

The table assumes a stoichiometric bulk density value for both the  $ZrO_2$  and  $Nb_2O_5$  films. There are a few different possible approaches to approximate atomic densities, in this case atomic mole fractions were used (mol/cm<sup>3</sup>). Notice that although

the IMFP for Si 2p is only around 5-8 nm and the overlayer thickness exceeds 10 nm, silicon concentration still reaches 10% at 5000 eV beam energy. It turns out that the brilliance of the synchrotron beamline is capable of generating strong enough electron signals to investigate buried environments deeper below the surface than the calculated IMFPs.

## 3.4.4 Conclusion

Though the changes are subtle from energy-to-energy, a wealth of information is provided in the HAXPES data. The above experiment demonstrates a proof of concept for probing thicker materials samples and more deeply buried environments. The challenge is to develop a scheme to explicitly assign a concentration profile with sample depths. A novel method for depth profile reconstructions, which builds upon the advanced XPS techniques discussed in this chapter, will be introduced in chapters five and six.

#### Chapter 4

# CHARGE AT THE INTERFACE OF A MOS STRUCTURE

This chapter will introduce the concept of a metal-oxide-semiconductor (MOS) material system and how charges located at the interfaces can be modeled using the advanced characterization techniques discussed in the previous chapter.

## 4.1 MOS Structure Introduction

MOS systems are the foundation for many integrated circuit devices, and, perhaps the most important is the metal-oxide-semiconductor field-effect transistor or MOSFET. MOSFETs are the switches in integrated circuits which relay digital information as a series of zeroes and ones by controlling conduction of current between the regions which are known as the source and drain (See Fig. 1.2, the sandwiched region is known as the gate which is composed of a MOS structure. Electrical conduction is mediated by an applied voltage to the gate metal, and because the oxide acts as an insulator charges are attracted to but not conducted across the semiconductor surface.

In the most simple model before any voltage is applied to the gate there are two assumptions made: the metal, oxide, and semiconductor in the MOS are in thermal equilibrium and no charges reside at any of the interfaces. At thermal equilibrium the metal and semiconductor in the MOS forms two plates of a capacitor separated by the thickness of the oxide[77]. Application of a voltage causes the system to depart from thermal equilibrium and induces charge to be stored on the capacitor. At one particular voltage value the applied voltage will exactly compensate for the potential difference between those two materials and electric fields in the oxide will disappear, this is referred to as the flat-band voltage  $V_{fb}$  and is the difference between the metal and semiconductor work function,  $\Psi_M$  and  $\Psi_S$  respectively:

$$V_{fb} = \Psi_M - \Psi_S \tag{4.1}$$

Often in practical systems the role of charges in the material stack cannot be ignored as in the ideal MOS. The existence of charges in the insulating oxide induces opposite charges in both the metal and semiconductor and alters the expected flat-band voltage. The existence of spatially separated opposing charges establishes a dipole effect and as a result impacts the expected energy band alignments. Though X-ray photoelectron spectroscopy is most sensitive to electrons from core levels they also track with the valence and conduction bands dependencies on spatially varying electric fields. It follows then that XPS techniques can be used to probe the electrical environments present in MOS stacks. In the following section the dipole affected band bending will be investigated using an advanced XPS technique[78].

# 4.2 Understanding the Role of Buried Interface Charges in a MOS Stack of Ti/Al<sub>2</sub>O<sub>3</sub>/Si using HAXPES

Ideally, deposited thin films would be studied in their unaffected, device ready state. Unfortunately, this approach makes chemical analyses of buried layers prohibitively difficult. There have, however, been advancements in synchrotron based photoemission techniques [79] and in conjunction with the continued scaling of devices, interfacial regions of multilayered films are within probing distances. Given the high brilliance and energy ranges of hard X-ray photoelectron spectroscopy (HAX-PES) chemical state as well as electronic information can be obtained non-invasively [69, 80, 73]. While numerous non-invasive elemental state analysis techniques like Raman spectroscopy, Auger electron spectroscopy (AES), or even standard X-ray photoemission spectroscopy (XPS), are available it may be difficult to quantify band alignments (Raman), or will be prohibitively surface sensitive without further sample modification (AES and XPS) [81, 82]. Exploiting the robust capabilities of HAXPES for elemental analyses and large probing distances allowed us to investigate the effects of oxide thickness on the band alignments within a metal-oxide-semiconductor (MOS) multilayer film. This technique is especially beneficial for modern electrical devices and chemical processes due to decreasing layer thicknesses and increasing importance of interfaces and energy band alignments. Our work demonstrates a powerful tool to elucidate the role that interlayer thickness plays in overall band alignments. With this in mind HAXPES could foster significant advancements in work function engineering as industry attempts to optimize each layer's performance by selectively introducing novel material compositions; a non-exhaustive search in relevant work function engineering literature can be found elsewhere [83, 84, 85].

Al<sub>2</sub>O<sub>3</sub> was chosen for its wide band gap [9] and usage in solar cells and transparent thin film oxides [86, 87, 88]. Ti was chosen as a low work function (WF) metal with WF of  $q\Phi_{m,vac}$ =4.33 eV [89].

## 4.2.1 Experimental

Al<sub>2</sub>O<sub>3</sub> films were deposited on 100 mm p-type (10-20  $\Omega$  cm) Si(100) substrates. Al<sub>2</sub>O<sub>3</sub> was deposited by atomic layer deposition (ALD) using trimethyl aluminum (TMA) and H<sub>2</sub>O at 300 °C in a Picosun showerhead ALD system. Deposited Al<sub>2</sub>O<sub>3</sub> thin films were 2 nm and 23 nm thick as determined by spectroscopic ellipsometry (not shown). Prior to Ti deposition, all samples were subjected to a thermal treatment of annealing (400 °C, 20 min) and firing (760 °C, 3 s). The firing step was similar to the one used for photovoltaics described elsewhere [54]. Ti deposition was carried out by evaporation using Cerac Ti pellets (99.8%) and a Thermionics VE-100 Vacuum Evaporator; deposition was carried out for 74 seconds at a rate of 0.07 nm/s as monitored by a quartz crystal microbalance (QCM) at a pressure of  $3 \times 10^{-6}$  Torr for a thickness of 5.2 nm. The uncapped 2 nm and 23 nm thermally treated samples will be referred to as 2-Al and 23-Al respectively, and Ti capped films will be referred to as 2-Ti and 23-Ti with numbers indicating the appropriate Al<sub>2</sub>O<sub>3</sub> thickness.

HAXPES experiments were carried out in ultra-high vacuum with end station pressure maintained below  $2 \times 10^{-8}$  Torr at National Institute of Standards and Technology (NIST) beam line X24A at the National Synchrotron Light Source at Brookhaven National Laboratory. Wavelength selection was carried out by a double Si(111) crystal monochromator; feedback-stabilization was also used to compensate for thermal effects on the crystals. The photon energy range available was 2.1-5 keV. Final focusing was carried out by nickel-coated quartz toroidal mirror. Nominal beam energy adjustment was referenced using a clean silver foil, and the Ag  $3d_{5/2}$  peak binding energy (BE) 368.3 eV [90] which was detected by a Scienta R4000 hemispherical electron energy analyzer located at a take-off angle of 85 °with a pass energy of 200 eV. We used a nominal photon energy of 4500 eV to excite core level electrons present in the Ti cap layer,  $Al_2O_3$ , and Si substrate. Strong signals from Al 1s and Si 1s core levels were present at this energy because of a large photoionization cross-section and were chosen over Al 2p and Si 2p levels for this reason. Like traditional XPS we deduced peak BE shifts and peak intensities to infer chemical states and energy band lineups. Approximate error associated with this measurement is +/-50 meV [70].

Differential charge correction is an important step in the analysis of XPS data, and for HAXPES data where photon energy may not be exactly known this step is especially crucial. In standard XPS, most X-rays are generated from either an Al or Mg filament which emit at known wavelengths 1486.6 eV and 1253.6 eV respectively. Often charge correction and photon energy is determined using elemental peaks from a clean metal surface. Unfortunately the challenge with this technique is that a previously calibrated monochromator position may be offset over time due to thermal loads from the synchrotron radiation on the monochromator, potentially skewing the energy reference.

We use a modified adventitious carbon peak energy referencing method [71] which can be used for future HAXPES studies. With a conductive channel to the sample surface to ground, elemental peaks from adventitious carbon and the silicon substrate were collected. Both of these reference spectra play a central role in our
analysis. First, let's consider peak referencing to the adventitious carbon peak. Adventitious carbon is a layer of material that is seen to deposit on many samples when exposed to the atmosphere; as a result the C 1s BE peak associated with this layer has been used with some success in the past. Of particular concern with this method is sample surfaces with high polarity, high density materials as in  $Al_2O_3$  [68]. Additionally, the adventitious carbon should be electrically isolated from the sample which may not be the case for a metalized surface [71]. To systematically correlate energy scales in each of our samples in this work we used the adventitious carbon C 1s peak to complement the Si 1s peak energy as the primary reference. A strong signal from the Si bulk was available for both the thin samples 2-Al and 2-Ti with our HAXPES probe; which previous work on similarly doped substrates assigned a value of 1839.5 eV [70, 69]. Shifting all peaks present in 2-Al and 2-Ti relative to their Si 1s peak, we now record the C 1s BE peaks as BE-Al and BE-Ti respectively, and notice that indeed BE-Al and BE-Ti differ by a value of 0.45 eV (See Fig.3.5). For the thicker samples 23-Al and 23-Ti the Si 1s peak intensity drops significantly and possesses an unacceptable signal-to-noise ratio, we then utilize the carbon C 1s peak collected from the thinner samples as a reference. Our complementary peak referencing method is outlined below:

- Set the Si 1s BE to 1839.5 eV for samples 2-Al and 2-Ti. Shift all XPS spectra from 2-Al and 2-Ti relative to the Si 1s shifts; record the C 1s BE as BE-Al and BE-Ti respectively. BE-Al and BE-Ti were found to be 286.15 eV and 285.7 eV respectively (Fig.3.5).
- Shift all spectra collected from sample 23-Al relative to the C 1s shift from BE-Al
- Shift all spectra collected from sample 23-Ti relative to the C 1s shift from BE-Ti

## 4.2.2 Results

Fig. 4.1 shows a representation of the deposited films (Fig. 4.1a) and the Al 1s core level spectra (Fig. 4.1b). The interfacial regions present after deposition are denoted as IL-1 and IL-2 for the oxide and Ti metal deposition respectively. Both 2-Al

and 23-Al show no BE shift within the error but BE shifts of -0.17 eV and 0.33 eV were seen post metallization for 2-Ti and 23-Ti respectively. Though 2-Al and 23-Al possessed the same BE, closer inspection of 2-Al reveals significant peak broadening compared to 23-Al (Table 4.1). First, it is important to point out the IMFPs at the photon energy used are around 4-5 nm [56]. And, because of inelastic scattering, the thinner oxide samples were probing more Al 1s electrons near the Si interfacial layer IL-1 than in the thicker film. Previous work eliminates the possibility of peak broadening by sub-stoichiometric aluminum oxides or the presence of phase changes for similar temperatures and deposition methods [55]. In that study they annealed ALD deposited  $Al_2O_3$  at three different temperatures (600, 800, and 1000 °C), noting interfacial growth and compositional changes; significant changes were only seen for the 1000 °annealed sample. Therefore, the conclusion made is that the broader peak width is indicative of an electric field on the  $Al_2O_3$  side of IL-1.



Figure 4.1: (a) Visual representation of the deposited films. Interfacial region IL-1 is present post-Al<sub>2</sub>O<sub>3</sub> deposition and IL-2 is present post-Ti deposition. Dashed lines represent the two different thicknesses of Al<sub>2</sub>O<sub>3</sub>. Not to scale. (b) Normalized Al 1s XPS spectra for samples 2-Al and 2-Ti (top) and samples 23-Al and 23-Ti (bottom).  $\lambda_{Al1s} = 5.58$  nm at photon energy  $h\nu = 4500$  eV.

The phenomenon initiating peak broadening of Al 1s peaks can be better understood by considering the electrical environment on the Si side of IL-1. Katamreddy *et* 



Figure 4.2: Si 1s spectra for 23 nm Al<sub>2</sub>O<sub>3</sub> before and after thermal treatments (annealing and firing). Peak intensities normalized to the elemental Si peaks to demonstrate increase in intensity of the satellite peak at 1843.5 eV, identified as the signal from SiO<sub>x</sub> interfacial layer IL-1.  $\lambda_{Si1s} = 4.83$  nm at photon energy  $h\nu = 4500$  eV.

al. reported that there was growth of a thin interfacial  $SiO_x$  layer after heat treatments similar to this study [55]. The thin  $SiO_x$  contained fixed positive charges, most likely because of oxygen vacancies [91, 92, 93]. The presence of these positive charges attracts negative charges from both the Al<sub>2</sub>O<sub>3</sub> and the Si substrate to IL-1, inducing dipoles on both sides. Confirmation of interfacial  $SiO_x$  growth is seen in Fig. 4.2 which shows the Si 1s spectra referenced to BE-Al for 23-Al before and after heat treatment. The silica peak (~1843.5 eV) for the thermally treated sample shows significant intensity increase relative to the elemental peak, proof of a thicker interfacial  $SiO_x$  layer. Additionally, the elemental Si 1s peak shifted -0.21 eV (referenced to BE-Al) after thermal treatments which can be explained by the presence of increased electron density at the surface of the substrate.

Metal deposition in our MOS structure created a second interface, seen in Fig. 4.1 as IL-2. After metallization there were three locations for charge accumulation: IL-1, IL-2, and the surface of the Si substrate. As discussed earlier the presence of positive charge near IL-1 attracts electrons. For IL-2 the proposed mechanism of charge transfer is known as the "second nearest neighbor effect". Electron density in

	Al	Al 1s				
Sample	$\begin{array}{c} \mathrm{BE} \\ \mathrm{(eV)} \end{array}$	FWHM (eV)				
2-Al 2-Ti 23-Al 23-Ti	$1562.64 \\ 1562.47 \\ 1562.66 \\ 1562.99$	1.85 1.89 1.67 1.82				

**Table 4.1:** Binding energy (BE) and full width at half maximum (FWHM) of Al 1score levels obtained for all samples

the oxide layer will increase because of the more electron donating nature of Ti relative to aluminum or oxygen [94]. There is also evidence of similar charge transfer in other metal-oxide systems [95].

The location of mobile charges as well as the proposed band diagram can be seen in Fig. 4.3. Presence of induced charges in the Al<sub>2</sub>O<sub>3</sub> does not necessarily preclude the existence of fixed charges, but is beyond the scope of the present study. To quantify the role of charges in this MOS system we need to consider the expected voltage drop across the oxide, known as the flat-band voltage. For the ideal case, which ignores charge in the insulating oxide layer, the flat-band voltage for a Ti metal and a p-type Si substrate is the difference between the Ti WF, 4.33 eV, and the Si WF,  $q\Phi_s =$ 4.87 eV [70]. Therefore, the ideal case would give a flat band voltage drop equal to  $q\Phi_{ms}=0.54$  eV.

It is possible to track the potential drop in the oxide by monitoring the photoemission peak shifts from that layer, in this case the Al 1s core level. The potential drop in our film stack demonstrated only a 0.33 eV BE shift in the Al 1s peak between samples 23-Al to 23-Ti (Fig. 4.1b) which is 0.21 eV smaller than the expected  $q\Phi_{ms}$ . The suggestion then, is to conclude the presence of negative charge in the Al<sub>2</sub>O<sub>3</sub> layer near the silicon interfacial region.



Figure 4.3: Energy band diagram for the uncapped thin 2 nm  $Al_2O_3$  film(a) and thick 23 nm  $Al_2O_3$  (b) and Ti capped thin (c) and thick (d) films. Gray areas denote location of mobile charge throughout the film stack.

Effects of negative charge in the oxide can be understood by decreasing the separation between IL-2 and IL-1, which will enhance electrical influence the two interfaces exert on each other. This situation is demonstrated in the Al 1s spectra of 23-Ti and 2-Ti, Fig. 4.1b. The metallic cap layer acts as a source of electrons so there would be an increased electron density in the Al<sub>2</sub>O<sub>3</sub> if the attraction is strong enough. The presence of increased electron density causes a BE decrease in 2-Al's Al 1s spectrum after metallization. This behavior is not observed in 23-Al because the film's Al 1s spectrum is dominated by the charge neutral bulk region. Combining the thin and thick film BE difference gives 0.52 eV (Table 4.1), which is in good agreement with the expected value of 0.54 eV. Given the decreasing thicknesses in material stacks used in modern devices the electrical and chemical processes taking place on smaller scales will play larger roles. In consideration of the present study, one could imagine work function engineering by only varying the thickness of the oxide. No other material or process changes would be needed. Already interfacial charges have been used for their beneficial screening and passivating properties [96, 93], HAXPES analysis would enhance the characterization of similar material systems.

## 4.2.3 Conclusion

In summary, we have used elemental HAXPES BE shifts to characterize the energy band alignment in a MOS stack of Ti/Al<sub>2</sub>O<sub>3</sub>/Si. The movement of the Al 1s core level before and after metal deposition indicated dissimilar potential differences across the thick oxide and the thin oxide interlayers. The dissimilarities are consistent with negative charges in the Al<sub>2</sub>O<sub>3</sub> layer accumulating near positive charges in the interfacial SiO<sub>x</sub>. This demonstrates the benefit of characterization techniques like HAXPES to probe buried material layers for electrical environments and chemical and elemental state analyses; thereby supporting the development of band engineering concepts.

### 4.2.4 Acknowledgments

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### 4.3 Future Work

Previously unavailable buried environments were elucidated by taking advantage of extended probing distances using HAXPES. Although the existence of mobile charges leading to dipole effects provides a convincing argument for unexpected band alignments, more supporting evidence could be found using a first principles approach. Unfortunately not enough information about the surface states in the silicon substrate, nor the magnitude of charge throughout the material stack was obtained. Correlating the HAXPES data presented here and first principles would be a strong case for using HAXPES as a primary characterization method for band engineering and interfial analyses.

### Chapter 5

# SIMULATED DEPTH PROFILES USING PROBABILISTIC CALCULATIONS

To calculate the distribution of atoms as a function of depth in lab based XPS systems often layers of material are removed by sputtering alternating with XPS surface scans. Sputtering is inherently damaging to the film and the resultant spectra will not necessarily represent the original film accurately. Compensating for sputtering one elemental species faster than another is especially challenging [97, 98, 99]. As a result, significant focus has shifted to the development of non-destructive techniques to generate compositional depth profiles (CDP) and avoid degradation of the samples.

Angle-resolved XPS (AR-XPS) is one non-destructive technique with a wealth of literature to draw from, see for example [71, 100, 101]. AR-XPS varies the take-off angle of the sample surface to the detector, which adjusts the probe depth by varying detected photoelectrons *transverse* path length through the film. Shallower glancing take-off angles increase the likelihood of inelastic collisions and decrease the likelihood of detection. A review by Cumpson discusses many of the statistical computational models deployed to recover CDPs from angle-resolved data [102]. Cumpson's report identifies the importance of regularization and linearization methods for accurate CMP transformations, yet admits that any reliable model hypotheses were fundamentally limited by the depth resolution of XPS.

Introduction of an additional non-destructive XPS experimental method known as variable kinetic energy XPS (VKE-XPS) overcomes inherent limitations of lab based XPS experiments [103, 100, 104]. Synchrotron based VKE-XPS selects incident X-ray beam energies which are capable of reaching higher photon energies thereby giving greater control to the photoelectron kinetic energy and thus the probability of detection. This study's experiments reached X-ray energies up to 5000 eV whereas more standard Al and Mg filament X-ray sources are only 1486.6 eV and 1253.6 eV, respectively. Ultimately, VKE-XPS technique is able to improve probing depths by an order of magnitude from around 2-3 nm to >20 nm [105].

Increased processing speed in modern computers now allows us to run calculations faster than ever, which has led to new and improved statistical methods for scientific modeling. Recent trends in other scientific domains take advantage of such increased computation capabilities to model experimental data using statistical techniques [106, 107]. This report features a comprehensive search algorithm, Bayes-Sim, that executes a "layer by layer" search to sample candidate CDP reconstructions. The framework Bayes-Sim uses to establish a belief system is known as Bayesian statistics. The Bayesian approach is used to calculate confidence values for reconstructed CDPs; this sort of construct for XPS data is introduced and discussed briefly in [108]. To increase the efficiency of the search Bayes-Sim uses a non-deterministic simulated annealing (SA) schedule. The SA schedule is a crucial implementation to avoid locally optimized CDP reconstructions. Interestingly, SA has been used for Rutherford backscattering experiments [109], but has not yet been applied to XPS. This work provides the first practical demonstration of a search algorithm based on a Bayesian formulation for XPS CDPs.

## 5.1 X-ray Photoelectron Spectroscopy

Fundamentally understanding how different XPS experiments can be correlated relative to each other is important for this work. How will the signal intensity vary as a function of take-off angle? How does the effective probing depth vary as a function of photon energy? For XPS much of this information is encapsulated into a relative sensitivity factor for each chemical species of interest. We will first introduce basic XPS concepts for relative composition quantitation and in the next section discuss how the Bayes-Sim algorithm adapts XPS data for a statistical framework.

### 5.1.1 Intensity Correction

Intensity correction using sensitivity factors for XPS data was introduced in section 3.4.1 and a similar approach will be used here. It is assumed that instrument specific parameters were constant throughout all VKE-XPS experiments and will therefore not contribute to sensitivity factor calculations. Each sensitivity factor (the denominator for each intensity correction - Eq. 3.9),  $R_A$ , for each chemical species, A, will therefore include three terms: elemental density  $n_A$ , photoionization cross-section  $\sigma_A$ , and IMFP  $\lambda_A$ :

$$R_A = n_A \sigma_A \lambda_A \tag{5.1}$$

## 5.1.2 IMFP Calculations

The IMFP value,  $\lambda$ , is used to estimate effects of scattering events on the path length for photoelectrons in a film. They will be estimated using the universal IMFP equation TPP-2M (Eq. 3.5). The material properties which are systematically calculated for each species IMFP value are: material density, band gap, molecular weight, and the number of valence electrons.

### 5.2 Bayes-Sim Search Methodology

Recently maximum entropy methods (MEM) were used to generate XPS compositional profiles with VKE-XPS for thicker films [101]. MEM is a modified least-squares fitting statistical technique which has been used for AR-XPS data. Weiland showed that MEM can be a powerful predictive tool with an accurate prior distribution and effective regularization methods. The Bayes-Sim method described in this report, though more computationally expensive, is a different statistical approach which introduces an explicit confidence value assigned to each simulation and improved data manipulation schemes.

#### 5.2.1 Bayesian Statistics and Hypothesis Testing

Bayes' theorem, though an old application of probability theory [99], has garnered interest as of late due to modern computational capabilities. Complementing experimentation by calculating model likelihood functions, this work establishes that Bayesian methods can be a useful modern predictive tool. The present Bayes-Sim formulation has been modeled on the framework described in [108]. In that report AR-XPS data was collected and established that reasonably accurate CDPs can be created for an appropriate depth scale. The present work expands on these results by introducing VKE-XPS simulations.

Informational terms will be organized into a set of matrices. Each of these matrices and their simulated configurations will be referred to using the following notation:

- [N] Relative atomic concentrations of species as a function of depth. Columns represent different chemical species, j, and each row represents a "depth slab", i, that are geometrically separated by a thickness  $\Delta t$  (Figure 5.1). Matrix elements must possess a value between 0 and 1.
- [D] Intensity corrected XPS intensities as a function of beam energy or angle. Columns represent different chemical species, *j*, and rows are separated by beam energies or angles, *k*.
- [λ] IMFP values as a function of beam energy or angle. Columns represent different chemical species, j, and rows are separated by beam energies or angles, k.

Bayesian likelihood calculations require known reference information to compare against simulated data. In this case the reference is experimental VKE-XPS data which will be encapsulated in the matrix  $[\mathbf{D}_0]$ . The first model or simulated fit to the data, called the prior, will be referred to as the matrix  $[\mathbf{N}_1]$ . Candidate priors  $[\mathbf{N}_2]$  are generated from whence simulated data  $[\mathbf{D}_2]$  and probability distributions  $P([\mathbf{N}_2]|[\mathbf{D}_0])$  can be calculated and tested against the prior's probability distribution,  $P([\mathbf{N}_1]|[\mathbf{D}_0])$ . In the end the final prior is referred to as the posterior and will be denoted as  $[\mathbf{N}_p]$ . Confidence values for each candidate prior are generated by collecting all the probability terms into the Bayesian formula :

$$P([\mathbf{N}_2]|[\mathbf{D}_0]) = \frac{P([\mathbf{N}_2]|[\mathbf{N}_1])P([\mathbf{D}_2]|[\mathbf{N}_2])}{P([\mathbf{D}_0])}$$
(5.2)

where  $P([\mathbf{N}_2]|[\mathbf{N}_1])$  is the probability distribution of the candidate CDP  $[\mathbf{N}_2]$  given the prior CDP  $[\mathbf{N}_1]$ ,  $P([\mathbf{D}_2]|[\mathbf{N}_2])$ , is the probability distribution of a simulated data set  $[\mathbf{D}_2]$  for the candidate CDP  $[\mathbf{N}_2]$ . The denominator,  $P([\mathbf{D}_0])$ , represents the probability of the experimental data set, which is a constant.

The two quantities in the right-hand side numerator of Eq. 5.2 are calculated assuming a normal distribution centered on a matrix element present in either the prior  $[\mathbf{N}_1]$  or experimental data  $[\mathbf{D}_0]$ :

$$P([\mathbf{N}_2]|[\mathbf{N}_1]) = \prod_{i,j} exp\left(\frac{-(n_{j,i} - m_{j,i})^2}{2\sigma_{Prior}}\right)$$
(5.3)

$$P([\mathbf{D}_2]|[\mathbf{N}_2]) = \prod_{j,k} exp\left(\frac{-(I_{j,k}^{calc} - I_{j,k}^{obs})^2}{2\sigma_{Data}}\right)$$
(5.4)

where  $n_{j,i}$  is a matrix element in the CDP matrix  $[\mathbf{N}_2]$  for species j and slab i,  $m_{j,i}$  is a matrix element in the prior reconstruction  $[\mathbf{N}_1]$ ,  $I_{j,k}^{calc}$  is a matrix element in the calculated data set  $[\mathbf{D}_2]$ , for species j and photon beam energy or angle k, and  $I_{j,k}^{obs}$  is a matrix element in the experimental data set  $[\mathbf{D}_0]$ . The values for  $\sigma_{Prior}$  and  $\sigma_{Data}$  are the variance contained in the prior and data distributions, respectively. The variance  $\sigma_{Prior}$  is input prior to executing the search algorithm and reflects the percent uncertainty one has in the atomic concentration matrix elements in  $[\mathbf{N}_1]$ . The  $\sigma_{Data}$ 



Figure 5.1: Layer-by-layer stack of *i* slabs with thickness  $\Delta t$ . Each slab in the stack is composed of homogeneous relative concentrations  $m_{j,i}$  of *j* species.

value is set to reflect the systematic variance during the chosen XPS experiment.

To transform the reconstruction  $[N_2]$  into  $[D_2]$ , a matrix of XPS intensities, the sample is modeled as a stack of slabs of thickness  $\Delta t$ . Photoelectron intensities for each slab and species are summed over all slabs by applying the Beer-Lambert as in [101]:

$$I_{j,k}^{calc} = \left[1 - exp\left(-\frac{\Delta t}{\lambda_{j,k}\sin\theta_k}\right)\right] \times \sum_i n_{j,i}exp\left(\frac{t_i}{\lambda_{j,k}\sin\theta_k}\right)$$
(5.5)

where  $\lambda_{j,k}$  is a matrix element in  $[\boldsymbol{\lambda}]$  for species j at beam energy or angle k,  $t_i$  is the sub-surface depth of slab i, and  $\theta_k$  is the take off-angle. Slab thickness is established by the initial prior.

### 5.2.2 Generating Candidate Priors

Bayes-Sim is a metaheuristic algorithm, it assumes that the exact global optimum value might not be found but an acceptably close solution can be. With this in mind, the role of the first prior is to begin calculations in an event space close to the global optimum reconstruction which also means judgment of the scientist is a crucial characteristic in this approach. Diversity of probability space sampling is executed by pseudo-random number generation. The search algorithm can be visualized as in Figure 5.2 for a 3x3 matrix reconstruction. The number of individual matrix elements changed is continuously reduced as are the variations from each absolute value. By scheduling an opportunistic algorithm, new priors will approach the global optimum reconstruction the closer the algorithm is to completion. Or, alternatively, exploration of the event space is needed most in the beginning but it is eventually mapped out by continuous random sampling.



Figure 5.2: Example of the iterative changes to the sampling routine operating on a 3x3 reconstruction. The elements are chosen randomly but notice the elements changed decreases with increased completion. O represents an un-changed matrix element, X represents a large change, Y is a medium change, and Z is a small change.

Transformation of a matrix element  $m_{j,i}$  into  $n_{j,i}$  is executed by:

$$n_{j,i} = m_{j,i} \pm \left( rand(\Delta x) * \left( 1 - \frac{\% complete}{100} \right) \right); n_{j,i} \in (0,1)$$
(5.6)

where rand $(\Delta x)$  is a random number between 0.1 and 0.5. The numerator "% complete" is the percent steps completed.

## 5.2.3 Sampling Routine: Simulated Annealing

Framework for simulated annealing (SA) algorithms can be traced back to work by Metropolis *et al.* in 1953 where they describe a method to calculate equations of state for interacting molecules [110]. Their work developed the concept of random sampling to calculate a large number of interactions in a many-body molecular system. Our SA schedule adaptation models an event space composed of many configurations of depth profiles  $[\mathbf{N}]$  to be randomly sampled.

In search of globally optimized outputs, calculations begin in a low probability configuration within the SA construct designated as high energy state  $E_{high}$ . Bayes-Sim must find paths to lower energy (higher probability) states, and if cooled slowly enough eventually reach the global minimum,  $E_{min}$ .  $E_{high}$  for Bayes-Sim is the initial prior reconstruction's probability distribution  $P([\mathbf{N}_1]|[\mathbf{D}_0])$  and  $E_{min}$  is the posterior reconstruction's probability distribution  $P([\mathbf{N}_p]|[\mathbf{D}_0])$ .

The role of the SA portion of the algorithm is to opportunistically replace  $[\mathbf{N}_1]$ with a candidate  $[\mathbf{N}_2]$  when the "cost" associated with the replacement is reduced enough to meet an acceptance criteria. The cost function will be the virtual energy step  $\Delta \mathbf{E} = \mathbf{E}([\mathbf{N}_1]) - \mathbf{E}([\mathbf{N}_2])$ .  $\Delta \mathbf{E}$  will be discussed in more detail in the following section. First let us consider how to proceed with the acceptance criterion of  $[\mathbf{N}_2]$ calculated by the acceptance probability function  $P_{accept}$ , or:

$$P_{accept} = exp\left[\frac{-\Delta E}{T_{SA}}\right] \tag{5.7}$$

The probability of acceptance is therefore dependent on the difference between the two simulated priors as well as the overall temperature in the system. Higher temperatures give "energy" to the SA construct so that  $[N_1]$  can be replaced with  $[N_2]$  even if the energetic cost is relatively large. It follows, then, that as the search continues to completion temperatures should slowly be lowered to eventually become frozen in the optimal configuration.

The key property of Eq. 5.7 is its non-deterministic nature. If we imagine a probability space like the one shown in Fig. 5.3 there are going to be locally optimized configurations,  $[\mathbf{E}_1]$ , which can act as traps. To hop out of locally optimized configurations the SA schedule must occasionally allow for jumps to higher energetic (lower probabilities) states like  $[\mathbf{E}_2]$ . Therefore, temperature profiles must decrease slowly enough to avoid local freezing but quickly enough to reach a frozen out global optimum by the end of the sub-routine loop.



Figure 5.3: Probability event space for simulated annealing. The algorithm assumes the initial conditions are in a high energy state which can only reach a global optimum by cooling the system slow enough to avoid local optimums by overcoming small energetic barriers (i.e.  $E_1 \rightarrow E_2$ )

### 5.2.3.1 Cost Function and Temperature Profile

Let us consider how both the cost functions and temperatures are explicitly calculated for Bayes-Sim. First, the cost in moving from  $[\mathbf{N}_1]$  to  $[\mathbf{N}_2]$  will be directly correlated with the Bayesian confidence values from Eq. 5.2. Assuming the probability distribution of  $[\mathbf{N}_1]$  is already known to be  $P([\mathbf{N}_1]|[\mathbf{D}_0])$ , then the cost to move to simulated depth profile  $[\mathbf{N}_2]$  is:

$$\Delta E = -\left(\log\left(P([\mathbf{N}_2]\big|[\mathbf{D}_0]\right)\right) - \log\left(P([\mathbf{N}_1]\big|[\mathbf{D}_0]\right)\right)$$
(5.8)

A log scale was chosen due to the enormous probability space encountered. It was not uncommon to begin with prior confidence values twenty or thirty orders of magnitude smaller than the posterior.

To maintain the generality of Bayes-Sim temperature profiles are determined only after an initial system temperature probe; each simulation must account for systematic differences between simulation with different variances or matrix dimensions. The initial temperature probe randomly generates one-thousand dummy  $[\mathbf{N}_{dummy}]$  reconstructions by again utilizing Eq. 5.2 to initialize the system temperature  $T_0$ , e.g.:

$$T_0 = -log(P([\mathbf{N}_{dummy}]|[\mathbf{D}_0])) \tag{5.9}$$

The lowest valued  $T_0$  is kept after one-thousand repetitions of Eq. 5.9 and a simple temperature profile maintains this system temperature, by default, at  $T_0$ until search completion reaches 50%; at which point the system temperature decreases linearly (see Fig. 5.4).



Figure 5.4: A Bayes-Sim temperature profile. An initial temperature  $T_0$  is set by the Bayesian formula, upon reaching 50% completion the system temperature decreases linearly.

The % complete is initialized by the starting conditions given by the user. If a user initializes Bayes-Sim for ten-thousand candidate priors the temperature profile will transition to the linearly decreasing profile after five-thousand candidates have been generated.

### 5.2.3.2 Bayes-Sim Process Flow

The full two-phase Bayes-Sim process flow has been realized as in Figure 5.5. The first phase acts only to set the system temperature before phase II initialization. Phase II carries out the candidate prior hypothesis tests, calculated by Eq. 5.2 and Eq. 5.7. The following paragraphs will detail a step-by-step guide for users of Bayes-Sim.



Figure 5.5: Two-phase Bayes-Sim process flow which transforms the initial prior  $[\mathbf{N}_1]$  into the posterior  $[\mathbf{N}_p]$ 

### Phase I - Temperature Probe

Initialization of Phase I begins when the user uploads the first prior  $[\mathbf{N}_1]$ , experimental data  $[\mathbf{D}_0]$ , appropriate IMFP values  $[\lambda]$ , and inputs the desired number of steps. New candidate prior reconstructions are generated using Eq. 5.6 and their confidence values with Eq. 5.2. Only if the confidence value of a new candidate  $[\mathbf{N}_2]$  is better than  $[\mathbf{N}_1]$  will the new system temperature be replaced using Eq. 5.9. Keep in mind that the initial prior  $[\mathbf{N}_1]$  will not be replaced during Phase I.

#### Phase II - Posterior Determination

Upon entering Phase II the system is set to a temperature  $T_{SA} = T_0$  from Phase I, and candidate reconstructions are generated once again with Eq. 5.6. New reconstructions, or depth profile simulations, are only kept if they pass the acceptance test Eq. 5.7. The final output reconstruction is kept as the posterior. Depending on the system properties Bayes-Sim behavior should rapidly probe vast areas of probability space in the beginning and slowly decrease the rate of prior substitutions due to the lower temperatures and proximity to the global optimum.

### 5.3 CDP Simulation with Bayes-Sim

The flexibility of Bayes-Sim makes it a useful tool to explore various geometrical and chemical properties of a sample. The flexibility also means that each simulation can be significantly different from previous ones with multiple parameter adjustments. Therefore, it is advised that only one degree of freedom is adjusted at a time. The following section will demonstrate model simulation dependencies on Bayes-Sim's degrees of freedom.

#### 5.3.1 Experimental

Simulations have been performed on 23 nm Al<sub>2</sub>O<sub>3</sub> films deposited by atomic layer deposition (ALD) using the organometallic precursor tri-methyl aluminum and H<sub>2</sub>O at 300°C. ALD consisted of two half cycles; in this case one half-cycle deposited a monolayer of metal (aluminum) and the other deposited a monolayer of oxygen. Al<sub>2</sub>O<sub>3</sub> layers were deposited on a silicon substrate. Thickness was measured by spectroscopic ellipsometry. Organometallic precursors can leave unwanted carbon contamination during ALD half cycles. Distinguishing between intermixed carbon and surface adventitious carbon in post-deposition characterization is an important indicator of *in situ* chemistry. For the current work, evidence of a 4-5% concentration of carbon atoms were detected at all photon energies, seen in Figure 5.6.



Figure 5.6: VKE-XPS Results: Photon energy versus relative intensity

VKE-XPS measurements were taken at the National Institute of Standards and Technology (NIST) beamline X24A at the National Synchrotron Light Source at Brookhaven National Lab. Photon energies of 2.5, 3, 3.5, 4, 4.5, and 5 keV were selected using a double Si (111) crystal monochromator. Wavelength selection and energy peak referencing was performed using the methods introduced in section 3.3 The sample surface to detector take-off angle was 85 °C for the present work. Simulated data will be compared to depth compositional analysis generated by ion sputtering the same film and collecting XPS spectra from a Physical Electronics 5600 XPS system which used a monochromated Al-K $\alpha$  excitation source; data collected from this system will hereafter be referred to as PHI-DATA. The PHI-DATA can be seen in Fig 5.7, it will be used as a model for the "ideal posterior", or the best case output for any simulation.

VKE-XPS peak intensities were calculated for the core electron levels of the C 1s, Al  $2p_{3/2}$ , O 1s, and Si 1s with Eq. 3.9. Peak areas were fitted using a Gaussian/Lorentzian product formula with a mixing coefficient of 0.3 and Shirley background subtraction. Calculated photoionization cross-section, IMFPs, and sensitivity factors for the species of interest are provided in Table 5.1.

Beam	Material	$C_{1a}$	11.9m	0.1	<b>C</b> ; 1.
energy	properties	$\bigcirc$ 1s	AI Zp	0.1s	51 15
$2500~{\rm eV}$	Photoionization cross section	3.0	1.49	8.09	63.59
	IMFP (nm)	5.03	4.47	3.78	1.64
	Sensitivity Factor	2.264	0.516	3.553	8.656
3000  eV	Photoionization cross section	1.82	0.67	5.66	39.88
	IMFP (nm)	5.94	5.2	4.53	2.5
	Sensitivity Factor	1.621	0.270	2.979	8.275
3500  eV	Photoionization cross section	1.04	0.41	3.17	26.12
	IMFP (nm)	6.84	5.92	5.27	3.3
	Sensitivity Factor	1.067	0.188	1.941	7.154
4000 eV	Photoionization cross section	0.72	0.23	2.36	16.94
	IMFP (nm)	7.71	6.63	5.98	4.07
	Sensitivity Factor	0.833	0.118	1.640	5.722
4500  eV	Photoionization cross section	0.48	0.16	1.51	13.82
	IMFP (nm)	8.57	7.32	7.69	4.82
	Sensitivity Factor	0.617	0.091	1.174	5.529
5000  eV	Photoionization cross section	0.35	0.1	1.16	10.0
	IMFP (nm)	9.42	8.0	7.38	5.55
	Sensitivity Factor	0.495	0.062	0.995	4.607

 Table 5.1: Estimated IMFP, photoionization cross-sections, and sensitivity factors used for Bayes-Sim calculations



Figure 5.7: Elemental distribution using sputtering cycles lasting one minute

## 5.3.2 Bayes-Sim Degrees of Freedom

Bayes-Sim methodology will be demonstrated by varying the adjustable degrees of freedom for simulations. It is important to realize that there are an infinite number of possible combinations and customizations that can be made to starting models and probablistic parameters like experimental variance or subroutine loops. As a result a comprehensive investigation for each system to be modeled is impossible. The predictive power of Bayes-Sim is that it complements previously held knowledge or discriminates observable differences between material samples, and it is up to the user to observe important distinctions. I will demonstrate this point by simulating the same experimental VKE-XPS data (Fig. 5.6) with many different initial conditions. The resultant qualitative and quantitative observations will then be discussed. Table 5.2, and Figs. 5.8-5.13 describe and present results for all simulations.

	ystem cool-down is the completion a. 5.9 and Fig. 5.4.	percenta	ge when the syste	m temperature $T_{\mathcal{I}}$	A begins its o	lescent, refer t
Simulation	0		Oxide	$\operatorname{Carbon}$	System	Confidence
Model	Description	Steps	Thickness (nm)	Thickness (nm)	Cool-down	Value
1A	Al:O:C Ratio 1:1:1 in bulk Carbon on surface	5,000	23.0	23.0	50%	$1.15 \times 10^{-8}$
1B	Al:O:C Ratio 1:1:1 in bulk Carbon on surface	50,000	23.0	23.0	50%	$5.09{ imes}10^{-6}$
2A	Dramatically thinner oxide	5,000	5.0	1.0	50%	$6.09\! imes\!10^{-10}$
2B	Dramatically thinner oxide	50,000	5.0	1.0	50%	$3.46 \times 10^{-7}$
3A	Thinner oxide	5,000	15.0	1.0	50%	$1.18 \times 10^{-9}$
3B	Thinner oxide	50,000	15.0	1.0	50%	$1.07 \times 10^{-8}$
4A	Differs from PHI-DATA with thicker carbon surface	5,000	22.0	2.0	50%	$2.17{ imes}10^{-5}$
4B	Differs from PHI-DATA with thicker carbon surface	50,000	22.0	2.0	50%	$1.59 \times 10^{-5}$
$5\mathrm{A}$	Initial prior which most closely matches PHI-DATA	5,000	23.0	1.0	50%	$1.36{ imes}10^{-2}$
5B	Initial prior which most closely matches PHI-DATA	50,000	23.0	1.0	50%	$4.48 \times 10^{-2}$

Table 5.2: Description of each CDP model, search algorithm parameters, and Bayesian calculated confidence values.



Figure 5.8: Each CDP model from Table 5.2 plotted against their posterior Bayesian confidence values.



Figure 5.9: Bayes-Sim simulated CDPs and confidence values for models 1A and 1B. Data for initial prior (line) as well as 5,000 step (dotted) and 50,000 step (dashed) simulations are shown.



Figure 5.10: Bayes-Sim simulated CDPs and confidence values for models 2A and 2B. Data for initial prior (line) as well as 5,000 step (dotted) and 50,000 step (dashed) simulations are shown.



Figure 5.11: Bayes-Sim simulated CDPs and confidence values for models 3A and 3B. Data for initial prior (line) as well as 5,000 step (dotted) and 50,000 step (dashed) simulations are shown.



**Figure 5.12:** Bayes-Sim simulated CDPs and confidence values for models 4A and 4B. Data for initial prior (line) as well as 5,000 step (dotted) and 50,000 step (dashed) simulations are shown.



Figure 5.13: Bayes-Sim simulated CDPs and confidence values for models 5A and 5B. Data for initial prior (line) as well as 5,000 step (dotted) and 50,000 step (dashed) simulations are shown.

### 5.3.2.1 Models 1A and 1B

Group 1 simulations used an initial prior which places carbon as a 1 nm adventitious layer and in the bulk of the oxide which has a stoichiometric ratio of 1:1:1 for carbon:aluminum:oxygen. The confidence values for these two simulations were on the order of  $10^{-8}$  and  $10^{-6}$  for the 5,000 and 50,000 step sub-routines, respectively; it will be obvious in the following discussion that these values are on the low end of our results thus far. Visually, the simulations are noisy without much coherence with our physical system - notice the abundance of silicon within the bulk oxide portion of the CDP.

### 5.3.2.2 Models 2A and 2B

These models possessed a thin oxide of 5 nm and carbon only on the surface. Simulation group 2 is a simple demonstration of the depth sensitivity of our technique. With the lowest confidence values and a chaotic posterior we have a strong indication that effective fits to our data should possess not only similar elemental abundances but appropriate layer thicknesses. The most striking feature of these simulations are that they no longer follows the distributions present in the initial prior, this is a unique quality compared to any of the following simulation groups. Clearly 2A and 2B can be eliminated as a viable model to the PHI-DATA.

### 5.3.2.3 Models 3A and 3B

Group 3 simulations modify the oxides thickness but keep the stoichiometry representative of bulk  $Al_2O_3$ . The thickness of the oxide was 15 nm in the initial prior. Bayesian confidence values are better than group 1 or group 2. These simulations are a good test to explore the depth resolution of our VKE-XPS data. If deeper layers of material were not contributing enough to the output intensities they would also weakly affect the Bayesian term from Eq. 5.4. Though, again, the posterior distribution does not match that of the PHI-DATA it is important to refer to our quantitative measure of "goodness".

### 5.3.2.4 Models 4A and 4B

Experiments for simulation models 4A and 4B use an initial model with a very thin surface carbon, a 23 nm oxide, but an Al:O ratio of 1:1. In an attempt to depart only slightly from the PHI-DATA model concentrations for the aluminum and oxygen was varied. Unfortunately these models were not able to transform into the data similar to the PHI-DATA despite their prior's CDP proximity to it. What is interesting to point out is that the overall confidence values are three orders of magnitude lower than the group 5 simulations, suggesting that although Bayes-Sim is unable resolve an effective posterior the confidence values will reflect that fact.

### 5.3.2.5 Models 5A and 5B

Group 5 models were built in an attempt to mimic the PHI-DATA as closely as possible. Initial priors for these models were all exactly the same. The difference between 5A and 5B is an increased number of steps 5,000 to 50,000, respectively. Both 5A and 5B have temperature cooling set-points at 50% completion. Even with increased number of steps Fig. 5.8 shows that these were all matched with Bayesian confidence values superior to all of the previous simulations. This suggests that Bayes-Sim can favor the "real" solution given good starting conditions. Increasing the steps only slightly improves confidence values as there is not much room for improvement beyond the initial prior.

## 5.3.3 Discussion and Conclusion

These five groups of simulations demonstrate a proof of concept for the Bayes-Sim algorithm. With VKE-XPS data (Fig. 5.6), and knowledge about the "real" system in question (Fig. 5.7) we were able to design the simulations with initial conditions close to and far from reality. Bayes-Sim is therefore most useful in situations where a fair amount of knowledge about a system or reference system is available. Unfortunately transformation from poor initial conditions into an accurate posterior model doesn't appear to be possible. There are two contributing factors for this. One is that the probability space is exceptionally large. It is not a question of only probing each probability event, but also contextualizing that event with all of the probability space around it. Second, and perhaps most importantly, there are multiple CDPs which can map onto the same VKE-XPS data. This is a result of the huge amount of CDPs possible and limited amount of contributions from each layer into the XPS intensity. The buried layers are especially challenging to model because of the surface sensitivity of XPS. These limitations are usually compensated by the user ensuring that simulations model a physical system and exploiting any previously held knowledge.

## 5.4 Final Remarks

Bayes-Sim, a new computational algorithm, has been developed to model compositional depth profiles from VKE-XPS and AR-XPS data. Bayesian calculations were used to assign confidence values to each model and a simulated annealing schedule was deployed to carry out the model sampling sub-routine. Five simulation groups containing different compositional models were used to reveal qualitative and quantitative behavior of Bayes-Sim simulations. The most likely simulation model closely matched that of the real system with a Bayes-Sim confidence value of  $4.48 \times 10^{-2}$ . For contrast, a poorly modeled initial prior revealed a Bayes-Sim confidence value eight orders of magnitude lower at  $6.09 \times 10^{-10}$ . In general higher Bayesian confidence values tracked with better initial conditions. The results indicate that it is not possible to map poor initial conditions onto a good posterior fit and as a result the usefulness of Bayes-Sim is somewhat limited by the knowledge of the user about the system.

### Chapter 6

## J-FAB: XPS ANALYTICAL TOOL AND SIMULATION SOFTWARE

### 6.1 Jon's Film Analysis for Buried Layers (J-FAB)

J-FAB is a new graphical interface built to support the Bayes-Sim optimization sub-routines introduced in chapter 5. There are four modules included in the J-FAB software package that includes: (1) Intensity Correction module calculates inelastic mean free-paths for photoelectrons generated in any material; (2) IMFP Calculator module calculates XPS sensitivity factors and correct XPS intensities for any elemental species at any energy; (3) VKE-XPS Depth Profile executes the Bayes-Sim search algorithm for VKE-XPS data; (4) AR-XPS Depth Profile executes the Bayes-Sim search algorithm for AR-XPS data. The flexibility to load search parameters, execute Bayes-Sim, and save the posterior distributions in modules (3) and (4) makes it easy to quickly run many simulations. J-FAB was developed in the programming language Python [107], which is able to construct a simple yet powerful graphical user interface (GUI) for complex mathematical operations. J-FAB is Windows based program. Documentation and program is available online as a stand-alone download [111]. Example simulation data are provided in the download.

## 6.1.1 IMFP Calculator Module

This module (Fig. 6.1) interfaces with the user to gather the necessary material properties to estimate IMFP values for any elemental species with the TPP-2M equation, Eq. 3.5. The required information is: species name, species binding energy (eV), photon energies used (eV), material density (g/cm<sup>3</sup>), band gap (eV), molecular weight (g/mol), and the number of valence electrons per molecule.

The TPP-2M to date is valid for electrons with kinetic energies between 50-30,000 eV. TPP-2M calculations are able to achieve accuracies below 10% [66]; and for the electron energies used in this study that provides a better than 1 nm accuracy for all elemental species. Stoichiometric bulk material densities and molecular weights are an acceptable approximation for many of the applications of J-FAB though a user is able to input any empirically derived values if desired. The band gap is only relevant for non-metals, otherwise it takes on a value of zero. Band gaps can also be approximated or experimentally determined. The number of valence electrons are either the number of electrons present in an elements outer atomic orbital for an elemental solid. For molecular compounds the number of valence electrons are the electrons involved in the chemical bond.

J-FAB IMFP Calcula le Help	itor					
		IMFP	Calculato	r		
Species	Photon Energy (eV)	IMFP (nm)	Density (g/cm³)	Band Gap (eV)	Molecular Weight	# of electrons
Add .	1 2 2 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5					
Add	1 2 2 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5					
Photon Energi	es Used: 0		Photon Energies	Calcula	ate	Save

Figure 6.1: IMFP Calculator GUI

### 6.1.2 Intensity Correction Module

The Intensity Correction module (Fig. 6.2) utilizes the methods introduced in section 3.4.1 to easily calculate XPS sensitivity factors for almost any material. Lab based XPS system sensitivity factors can be looked up and inserted into the module directly or the user can input individually calculated parameters for each elemental species. Recall that a sensitivity factor R calculation includes approximations for: elemental density n, photoionization cross-section  $\sigma$ , IMFP  $\lambda$ , angular anisotropy  $\Theta$ , X-ray flux f, X-ray probe area A, and the detector's transmission function T. For most XPS experiments it is the material properties which are most likely to change and they will therefore be the only components included in this module.

Similar to the IMFP Calculator the user should be able to make accurate approximations with limited knowledge about the material system. Photoionization crosssections are calculated as a function of beam energy from [75, 76]. IMFPs can be directly loaded from the IMFP Calculator module. The mole fraction is an estimation of the *elemental* density, which is an important distinction from the material density. Other parameters like the element's atomic radius could suffice for this calculation; both parameters are easily looked up in reference materials.

			Intensit	y Correction			
Species	Photon Energy (eV)	Raw Intensity	Mole Fraction (mol/cm <sup>3</sup> )	Photoionization Cross-section	IMFP (nm)	Sensitivity Factor	Corrected Intensity
Add	2						
:	3 4 5						
Add	2						-
:	3						

Figure 6.2: Intensity Correction GUI

### 6.1.3 VKE-XPS Depth Profile and AR-XPS Depth Profile Modules

The simulation modules can simulate up to six individual species and require three input files to begin calculations: (1) *Data File*; (2) *Prior File*; (3) *IMFP File*. The *Data File* is the sensitivity factor corrected data arrays from an XPS experiment, which also transfers the individual species and binding energies. The *Prior File* is a user



Figure 6.3: The VKE-XPS Simulation module.

generated depth profile used as the starting point for the Bayes-Sim search algorithm. The *IMFP File* calculates IMFP values for all species of interest included in the *Data File* and *Prior File*. Both *Data File* and *IMFP File* inputs can be generated using the Intensity Correction Module and the IMFP Calculator Module, respectively.

Once the three input files are uploaded, the user may enter parameters needed for the search algorithm. Following the GUI layout shown in Figure 6.3, the section named "Species Used" provides a few options: the user can set a limit for the minimum or maximum depth which a species is present.

The user can specify the accuracy of the experimental measurements and the initial prior by adjusting the following variance values:

- $\sigma$  (Data) intensity variance in *Data File*
- $\sigma$  (Prior) atomic concentration variance in *Prior File*

Another customizable user parameter is the "Initiator" percentage. The initiator allows the user to choose the temperature cool-down set-point, in other words this value initiates the simulated annealing temperature to transition from its constant value of  $T_0$  calculated from Eqn. 5.9 into the linearly decreasing function represented by Fig. 5.4.

On the lower right part of the GUI the user can set the maximum number of steps, with a minimum of 1000 as required by the search algorithm. The value  $\theta$  is the take-off angle (the angle between detector and sample surface). This box is disabled for AR-XPS simulations but must be set for VKE-XPS simulations.

The graph window has the option to display two different simulated profiles. The "Best" button displays the strongest CDP candidate based on its confidence value. The "Average" button displays a collective average of all the replaced priors found during the search, this is an especially useful function to estimate each species' and each slab's standard deviation. Standard deviation values are provided in the saved file. Quality of the initial prior model is evaluated by the final posterior's probability distribution or confidence (Eqn. (5.2)) which is displayed in the upper right of the module's window Figure 6.3.

### 6.2 J-FAB Credits and User License Agreement

### **J-FAB** Credits

The interface portions of J-FAB and modules were developed by Jonathan Church at the University of Delaware. Special credit also belongs to Conan Weiland at Synchrotron Research, Inc for establishing the framework of a Bayesian search algorithm, and the functions deployed within the search algorithm to manipulate x-ray photoemission spectroscopy data.

## J-FAB License

J-FAB is Open Source (http://opensource.org/) software. You are free to use, modify, and redistribute the source code and documentation. There is no charge for their use. The main limitations are that you cannot claim you wrote the program or documentation and cannot prevent other people from using them.

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# Chapter 7 SCIENCE IN ART

Recently, advanced material characterization methods have been applied to the study of paint pigments taken from iconic artworks of the past. In an attempt to curtail obvious signs of degradation (i.e. discoloration, spalling, cracking, etc.) museum curators and preservationists need to investigate the relevant chemistries present in their paintings. Often the first chemical clues, other than visual inspections, are revealed by the time period techniques used in which the painting was created. The development of oil paintings enabled more vibrant blues and reds to be applied to canvases, for example. On the other hand chemicals like mercury, lead, or arsenic become exceedingly rare due to public health concerns. Next, restorative efforts might consider the artists individual color recipes; how the pigments were mixed with binders, fillers, and dispersants. Finally, it is important to consider the painting's storage environment, especially the use of protectants or exposure to exceedingly bright or damp conditions.

Motivation for "Science in Art" investigations begins with the curators. There may only be a few individuals in the world with detailed knowledge of the artwork and intimate access to it. Scientific research efforts are usually called upon when historical knowledge and visual inspections are insufficient to preserve a work; new micrometer spatial resolution techniques have lead to better understanding of the micro-structure of the pigments and hopefully a better understanding of degradation of these important pieces of artwork.

The superior capabilities of synchrotron based spectroscopies will be exploited for chemical mapping and micro-structure analysis in the following chapter. Our collaborative efforts with the Barnes Foundation in Pennsylvania, Winterthur Museum in Delaware, and the University of Amsterdam in the Netherlands have provided the opportunity to study the paint pigments from: cadmium yellow in *Le Bonheur de vivre* by Henri Matisse (1905-1906) and arsenic sulfides from 18th century works.

#### 7.1 X-ray Absorption Spectroscopy (XANES)

X-ray absorption near-edge spectroscopy (XANES) and near-edge X-ray absorption fine structure (NEXAFS) are methods to probe electronic transitions of the present elemental constituents using X-rays. Incident X-ray energies are scanned and, depending on the studied material, sharp increases in X-ray absorption will appear at different energies. Relaxation after X-ray absorption leads to fluorescing from the excited atoms, and can elucidate information about the surrounding atoms and chemical species. In fluorescence, X-rays excite core level electrons to higher-energy states, where the newly freed atomic core-levels will be quickly filled by other electrons, creating a measurable fluorescence spectrum (see Fig. 7.1). The resultant fluorescence spectrum will be dependent on the nearby density of states provided by the surrounding chemical environment, which means chemical species can be uniquely identified.





Figure 7.1: Two step XANES process. Step 1 (left) is the photoemission of an electron from energy state  $E_n$  after X-ray absorption. Step 2 (right) is the emission of a photon with energy  $E_{n+1}$  -  $E_n$ 

The "pre-edge" and "post-edge" features in XANES spectra are the fingerprints for different chemical constituents ("edge" refers to the onset of strong X-ray absorption within the sample). Those distinguishing features of spectra collected from sample materials are usually compared against known reference standards. Consider Fig. 7.2 which illustrates a XANES spectrum collected at the Cd  $L_{III}$  absorption edge (3.52-3.64 keV). The strongest intensity, the "white line", appears at 3568 eV, with two strong pre-edge features, and a minor post-edge feature located around 3580 eV. Combined, these features and those present in other standards demonstrates a simple yet powerful characterization method.



Figure 7.2: XANES and NEXAFS spectrum of  $CdCO_3$  powder reference standard showing the distinguishing pre-edge, post-edge features as well as the maximum absorption energy, or white line.

#### 7.2 Sample Composition Using Least Squares Fitting

In many cases sample target locations are composed of multiple chemical species and will therefore exhibit XANES features from each of the excited species. By collecting XANES spectra for multiple reference standards target data can be fit to a linear combination of standards. The software package used in this work for least-square fitting was SixPACK [112], and will briefly be discussed. Three different SixPACK modules were used: "SamView", "Background Removal", and "Least Sq. Fitting". SamView was used to view, import, and save the raw data from the synchrotron beam line in a SixPACK compatible format. The Background Removal module was used to correct and normalize data to a common intensity scale. Finally, the Least Sq. Fitting module allows users to upload and fit data for a sample target location, and multiple candidate standards. Output of the Least Sq. Fitting module provides an estimation of the abundance for each given standard and an overall  $\chi^2$  value for each fit. Addition and deletion of candidate standards is performed by interfacing with the software.

#### 7.3 Photodegradation in Matisse's Cadmium Yellows

Le Bonheur de vivre is a large - 176.5 cm  $\times$  240.7 cm (69.5 in  $\times$  94.75 in) postimpressionist era work, painted with oil on canvas by the artist Henri Matisse. Visual inspection of *Le Bonheur de vivre* revealed a discoloration in what were previously yellow regions. Matisse in this particular painting used two types of yellows; one was chromium based and the other cadmium. The brighter, more vibrant chromium yellow has maintained its character over time, however, the cadmium yellow from cadmium sulfide (CdS) which originally was a warmer pale yellow has become either an ochre-like tan or off-white color. The painting and its chromium or cadmium yellow locations have been identified in Fig. 7.3.

Notably, work by Leone *et al.* concluded that many of the artworks also using cadmium yellow pigments have exhibited color degradation [113]. Their hypothesis was, because of photo-oxidation, the cadmium sulfide underwent a chemical reaction leading to the discoloration. Their hypothesis could be confirmed by the presence of photo-oxidation by-products like  $CdSO_4$ ,  $CdCO_3$ , CdOH, or cadmium carbonate. Identification of these species in the degraded paint layers are made possible by spectroscopic studies such as XANES, and will therefore be used to elucidate the chemical mechanism behind the photodegradation of Matisse's cadmium yellows.



Figure 7.3: Henri Matisse's Le Bonheur de vivre, The Barnes Foundation, BF719, Philadelphia, Pennsylvania, USA. Yellows are identified as either Cr or Cd based depending on their elemental composition. Three samples S113 (upper-left foliage), S5 (middle), and S115 (fruit in trees) were obtained and analyzed in this work.

#### 7.3.1 Experimental

Fig 7.3 identifies the location of samples from three degraded yellow areas of *Le Bonheur de vivre*: the upper left foliage (S113), below the central reclining figures (S5), and the fruit in the tree on the right-hand side of the painting (S115). Also, reference standards of cadmium sulfide (CdS, 99.995 % metals basis), cadmium oxide (CdO, > 99.99 % pure), cadmium sulfate (CdSO<sub>4</sub>), cadmium chloride (CdCl<sub>2</sub>, > 99.99 % pure), CdOH<sub>2</sub>, and cadmium carbonate (CdCO<sub>3</sub>) were used for XANES least-squares fitting and chemical mapping. Each sample was mounted in a polyester resin from Extec Corporation( $\hat{\mathbf{R}}$ ). Reference standards were finely spread on an adhesive tape.

Beamline ID21 at the European Synchrotron Radiation Facility (ESRF) was

used for the cadmium  $L_{III}$ -edge (3.52-3.65 keV, step size = 0.3 eV) XANES analysis. A fixed exit Si(111) crystal monochromator was used to adjust X-ray beam energy which was then focused for  $\mu$ XANES with Fresnel zone plates to a spot size of approximately  $0.3 \times 0.7 \ \mu m^2$  for experiments using the Cd  $L_{III}$ -edge. The beamline was operated under vacuum conditions.

XANES chemical maps were obtained using PyMca software. Chemical species spatial distributions were obtained by setting incidence X-ray energies at a particularly sensitive fluorescing energy for that species and scanning the exposed cross-sectional areas of the samples. Regions of interest (ROI) for XANES points were chosen by correlating locations with different compositions and cross-sectional photomicrographs.

#### 7.3.1.1 Regions of Interest

Each of the samples S5, S115, and S113 measured approximately  $100 \times 200 \ \mu m^2$ . The spatial resolution of the X-ray spot size of  $1 \ \mu m^2$  enabled the collection of many different  $\mu$ XANES spectra from one sample. To efficiently collect the desired  $\mu$ XANES spectra an efficient experimental procedure needs to be followed. The first concern is maximizing beamline usage; beamline time can be competitive and once time is awarded users will use the beamline station almost continuously once started. There is also the concern of beam "down-time" which is out of the user's control and can span hours or even days. With this in mind I have followed a standard operating procedure to best take advantage of the X-ray probe availability. The following results and discussion rely heavily on strict adherence to this procedure:

- 1. Focus on sample area to be studied and adjust X-ray to energy which 6excites all interested species
- 2. Ensure proper beam alignment, focusing, and calibration
- 3. Scan over the surface area of the sample to create a wide-area chemical map and correlate with photomicrographs
- 4. Identify, record, and save spot locations with elements of interest. For example, the ground layer (the priming layer which acts as a substrate for the paint

pigments) in these samples was identified by a homogeneous mixture of barium sulfates and lead, and was therefore given lower priority. On the other hand areas with high concentrations of cadmium or islands of sulfur were given higher priority.

5. Move to those saved ROIs and collect  $\mu$ XANES spectra at those locations.

#### 7.3.2 Results and Discussion

Photomicrographs and chemical maps of samples S5, S115, and S113 are shown in Figs. 7.4 and 7.5. The most heavily scrutinized areas were located in the brown interfacial regions seen in the visible micrographs between the cadmium yellow layer and the white ground; the hypothesis being that the brown region is representative of the degrading paint layers. XANES wide-area chemical maps revealed an abundance of cadmium still present in the samples and scattered sulfur islands located in the supposed degraded regions. In an attempt to distinguish the distribution between different chemical species or relative abundances XANES data was collected for both sulfur rich and sulfur poor locations.



Figure 7.4: Visible and ultra-violet photomicrographs of samples S5 (a), S115 (b), and S113 (c). The ground layer can be seen as a white region in the visible micrographs. Printed with kind permission from Springer Science and Business Media: Springer Applied Physics A/"The photodegradation of cadmium yellow paints in Henri Matisse's Le Bonheur de vivre (1905-1906)", 111, 2013, 59-68, Jennifer L. Mass, Robert Opila, Barbara Buckley, Marine Cotte, Jonathan Church, Apurva Mehta, Fig. 2



Figure 7.5: Wide-area XANES chemical maps for samples S5 (a), S115 (b), and S113 (c). Locations of μXANES points are numbered for each sample. Notice the gray band in (b) caused by the loss of beam during the scan. Strong sulfur (blue) signal in (c) comes from the barium sulfate ground layer.

By collecting the ROI from samples S5, S115, and S113 a representative average abundance of each chemical species in the samples can be determined by fitting a linear combination of each of the six reference standards' XANES spectra to a single XANES point. For example, see Fig 7.6 which shows a data point from sample S5 and point 8 (Fig 7.5a); the characteristic features are visible in each of the reference spectra. It appears that this particular point's spectrum has a white line which is shifted in energy from the CdS white line, but possesses strong carbonate features. The statistical weight of each standard spectrum provided an estimated concentration

Sample	$\mathrm{CdCO}_3$	CdS	$\mathrm{CdCl}_2$	CdO	$\mathrm{CdSO}_4$	$\mathrm{CdOH}_2$
S5	63.94%	23.82%	8.30%	2.95%	$<\!1\%$	<1%
S115	53.59%	15.30%	7.37%	6.86%	16.88%	<1%
S113	50.52%	13.46%	7.53%	<1%	23.54%	4.95%

Table 7.1:Representative relative concentrations for cadmium species in samples S5,<br/>S115, and S115. Calculated using XANES peak fitting software.

in the chosen data point. Concentrations for all  $\mu$ XANES points and a given sample were then summed and averaged for each sample, giving a representative sample concentration. Table 7.1 shows the results from data collection on the Cd  $L_{III}$ -edge for all three of the samples, giving relative concentrations approximated using the Six-PACK XANES peak deconvolution software. These results suggest that the greatest constituent was  $CdCO_3$ . This also confirms previous XPS studies performed on the same sample (not shown)[114]. Though this seems to support the photo-oxidation mechanism proposed by Leone *et al.*,  $CdCO_3$  is also known to have been a common filler material and therefore does not conclusively support photo-oxidation degradation [115]. The consistently large abundance of  $CdCO_3$  over all other species would also support the hypothesis that the carbonate was used as filler. Unsurprisingly, each of the samples still possesses a significant amount of the original vellow CdS compound. Evidence of the cadmium yellow wet-process synthesis is seen in the consistent, though moderate, chloride concentration for each of the samples;  $CdCl_2$  is known to be a common starting reagent for CdS yellow. Presence of cadmium sulfate in S115 and S113 could be a good indicator of the photo-oxidation process.

If we consider each of the chemical maps in Figs. 7.5(a-c) and Table 7.1 there are two conclusive observations that can be made regarding degradation occurring in *Le Bonheur de vivre*. First, it is clear that Matisse was using CdCO<sub>3</sub> as a white filler material in the paint pigment. Nearly all  $\mu$ XANES spectra collected possessed a CdCO<sub>3</sub> like fingerprint, and deconvolution of the data points quantitatively support this as compositions possessed a majority of CdCO<sub>3</sub>. If CdCO<sub>3</sub> was a by-product of



Figure 7.6: Standards and an S5 point  $\mu$ XANES spectra. Vertical dotted lines from show a few distinguishing features present in the CdCO<sub>3</sub> and CdS spectra.

the decomposition sample it would be indistinguishable from the filler. Second,  $CdCl_2$  is likely present from the synthesis method to make CdS paints. It is present in similar relative abundances throughout each of the samples and is widely spread through the layers. From this information we can gather that the CdS was premixed with other cadmium containing compounds.

At this point the degradation mechanism cannot be conclusively stated, but there is enough evidence to eliminate the two by-products CdO and CdOH<sub>2</sub> from that mechanism. CdO was initially considered a probable compound resulting from degradation as it is brown and the degraded yellow regions in *Le Bonheur de vivre* have taken on a brown-ish tint. The strongest degradation marker so far is the presence of CdSO<sub>4</sub> in larger abundances. More reading on this work which the author has contributed to has been published elsewhere by Mass *et al.*[114], where it was posited that  $H_2SO_4$  is likely the by-product of reactions with atmospheric  $H_2O$  and  $CO_2$ :

$$CdS + 2O_2 + H_2O + h\nu \rightleftharpoons CdSO_4 \cdot H_2O$$
 (7.1a)

$$CdSO_4 \cdot H_2O + CO_2 \rightleftharpoons CdCO_3 + H_2SO_4$$
 (7.1b)

#### 7.3.3 Conclusions

Three samples from degrading yellow areas from Henri Matisse's *Le Bonheur* de vivre were extracted. The yellow pigments, associated with a CdS compound, were studied using X-ray absorption near-edge spectroscopy (XANES) to elucidate chemical compositions and distributions. Using a least squares fitting technique available with computational software  $\mu$ XANES data points were collected at different regions of interest (ROI) and fit to a linear combination of six references of standard chemical compounds. The reference standards CdCO<sub>3</sub>, CdS, CdCl<sub>2</sub>, CdO, CdSO<sub>4</sub>, and CdOH<sub>2</sub> were used. It was discovered that CdCO<sub>3</sub> was found in the greatest abundances of >50% in each of the three samples. CdCl<sub>2</sub> was also found to exist in each of the samples at relative concentrations around 7-8%. CdCO<sub>3</sub> is likely associated with paint filler but is also proposed to be a degradation by-product. CdCl<sub>2</sub> is a likely synthesis reagent. CdSO<sub>4</sub> was also discovered in significant abundance and is a proposed photodegradation by-product.

## 7.4 Transformation of Arsenic Sulfide Pigments from early 18th Century Works

Some arsenic sulfide minerals were highly sought after by European artists in the 18th century owing to their full and vibrant colors. Realgar and orpiment are two common names for the arsenic sulfides  $As_4S_4$  and  $As_2S_3$ , respectively. Realgar crystals are a vibrant, translucent red material whereas orpiment, though chemically similar, takes on a deep yellowish-orange color. Before the harmful side-effects of arsenic paints were discovered, realgar and orpiment were commonly crushed into powder form to be used as pigments in classic oil paintings or for ornamental motifs. In this section I will discuss scientific investigations of an 18th century work which appears to have lost degrading over time as a result of photo-oxidation.

#### 7.4.1 Introduction

Photo-induced transformations cause a realgar pigments phase change into a compound called para-realgar and takes on a yellow color [116, 117, 118]. Orpiment on the other hand decomposes into colorless arsenite  $(As_2O_3)$  [118]. With regards to the use of realgar in paintings the transformation is likely to cause cracking and crumbling in degradation areas. *Still Life with Five Apricots* by Adriaen Coorte has shown some of the classic examples of realgar degradation (Fig. 7.7); there is friable material along the cracks of the orange-ish regions in the apricots and significant fading. Similar techniques used to study Matisse's *Le Bonheur de vivre*, XANES chemical maps and spectra deconvolution will be used to understand the mechanisms behind these material decompositions.

Further reading for this work which the author contributed is available elsewhere [119].

#### 7.4.2 Experimental

A sample from *Five Apricots* was encased in polyester resin Polypol PS230 using the Easysection<sup>TM</sup> system and dry polished with Micro-mesh ( $\mathbb{R}$ ) polishing cloths.

XANES experiments were carried out at beamline 2-3 at the Stanford Synchrotron Radiation Lightsource (SSRL), a directorate of Stanford Linear Accelerator Center (SLAC) and an Office of Science User Facility operating for the U.S. Department of Energy Office of Science by Stanford University. Beamline 2-3 has a bending magnet side station for X-ray imaging and X-ray absorption spectroscopy studies. A Kirkpatrick-Baez mirror system was used to achieve focused spot sizes of  $2 \times 2$  $\mu$ m<sup>2</sup> for  $\mu$ XANES data collection. The monochromator was a double crystal Si(111) and can scan energy ranges between 5-24 keV. The arsenic K-edge XANES spectrum



**Figure 7.7:** Still Life with Five Apricots by Adriaen Coorte (1704), Royal Picture Gallery Mauritshuis, The Hague, The Netherlands.

was collected between an energy range of 11855-11890 eV. Experiments were carried out in ambient conditions, and samples were held in place with double-sided tape (Scotch  $(\mathbb{R})$  tape). XRF chemical maps of *Five Apricots* were collected at an X-ray energy of 13 keV. Reference standards used were realgar (Sigma-Aldrich 95%), As<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich 99.995 %), and As<sub>2</sub>O<sub>5</sub> (Sigma-Aldrich 99 %). An orpiment reference standard XANES spectrum was also collected but was not unambiguously distinguished from the realgar spectrum.

Regions of interest were chosen following the procedure described in section 7.3.1.1.

#### 7.4.3 Results and Discussion

Fig. 7.8 shows XRF images of a cross-sectional of *Five Apricots*. The three colors represent arsenic (green), sulfur (red), and lead (blue). Lead was known to be a common ingredient used in ground layers. It appears that the degraded upper layer, deficient of arsenic, is resting on an intact region of paint with paint particles clearly visible. To establish a representative chemical speciation throughout these layers  $\mu$ XANES data will be collected for locations 1-3.



Figure 7.8: Cross-sectional XRF map from *Five Apricots* showing four different locations (marked by a cross-hatch) for  $\mu$ XANES, arsenic (green), sulfur (red), and lead (blue) are represented by their different colors. Three distinct regions are visible: degraded paint layer (3), intact paint particle (1) and the ground layer (2 and 4).

One of the key questions to answer for this study was how the degradation influenced the distribution of by-products throughout the paint layers. From Fig. 7.8 it appears that leaving groups containing arsenic either migrate out of the paint layers or towards the ground layer. It turns out that arsenic oxide species are mobile in the presence of water[120], and as a result in high relative humidity conditions could cause arsenic migration. This behavior can be seen if we consider the results shown in Fig. 7.9. The figure shows the  $\mu$ XANES spectra for three different paint layers (black) and compares them to the three reference standards (red). If we consider the intact spectrum it shows a very strong realgar fingerprint; confirmation that the intact particle has not undergone oxidation. However, spectra from locations (2) and (3) have a second peak located at the same energy as an arsenate peak,  $As_2O_5$ . Closer inspection of the spectra for points (2) and (3) reveals a disparity between the two oxidized regions also exists. In (2) the arsenate to realgar peak intensity ratio is significantly reduced compared to (3), suggesting that the exposed altered region has undergone a greater amount of oxidation.



Figure 7.9:  $\mu$ XANES As K-edge spectra for locations 1-3 seen in Fig. 7.8 (black) compared to XANES spectra for the reference standards (red): (1) intact spectrum (left), (2) paint/ground interface (middle), and (3) altered layer (right). Vertical lines are the energies of the XANES heat maps shown in Fig. 7.10.

Somewhat surprising is the lack of arsenite  $(As_2O_3)$  features in the  $\mu$ XANES spectra. Thermodynamically, arsenite is the final oxidation product of realgar and therefore should be abundantly present. To observe the distribution of arsenite species we can systematically excite those species by adjusting the X-ray energy. Refer to the reference standard spectra shown Fig. 7.9; scanning the surface with X-rays at energies where the unique features of each standard are maximized will highlight the regions containing those species. For example surfaces scanned with lower energies below the rising edge should only reveal locations of intact realgar as the oxidized species have features at higher energies. Figs. 7.10(A-D) show these type of XANES "heat maps" which have been collected at different X-ray beam energies. Greater absorption is correlated with redder regions and increasing X-ray energies are shown going from: A) 11865 eV to B)11869 eV to C) 11875 eV to D) 11901 eV. Indeed Fig 7.10(A) is dominated by the intact regions of the paint sample. Fig. 7.10(B) shows the location of realgar paint and most likely some contributions from arsenite. Fig. 7.10(C) is the maximum intensity for arsenate and shows a distinguishing feature along the interface with the ground and a major increase in intensity is also seen towards the altered layer (top) in the middle of the image.



Figure 7.10: XANES "Heat maps" of the *Five Apricots* cross-section at different X-ray energies, oranges and reds highlight areas that are most strongly absorbing X-rays. X-ray energies used are: A) 11865 eV, B) 11869 eV, C) 11875 eV, and D)11901 eV.

To summarize, the heat maps show the arsenite species affinity to remain localized around the intact paint particles while the more oxidized arsenate gathers further away. If we imagine that the arsenite species become mobilized in an aqueous environment they would tend to collect at the interfaces or surfaces. Because of the presence of different species from the ground layer or ambient atmosphere those arsenite species further oxidize to arsenate.; there is evidence in the literature that arsenite can oxidize to arsenate in aqueous solutions [121, 122]. Still, it is not clear why the arsenate exists near the altered regions and ground layers and the arsenite remains localized to the intact particles. It is likely due to the local chemical environment near the ground layer and surface altered region but more study is needed to understand these influences.

#### 7.4.4 Conclusion

Chemical speciation and distribution of arsenic pigments within the 18th century work *Still Life with Five Apricots* have been studied using XANES. The oxidized arsenic species arsenite  $(As_2O_3)$  and arsenate  $(As_2O_5)$  were both observed throughout the degraded sample areas and are most likely correlated with the degradation of the paint observed in the apricots. Arsenate appeared to be in greater abundance in the altered surface regions and interface with the ground layer whereas the arsenite remained localized to the intact paint pigments. This is partly explained by the mobilization of arsenite away from the paint towards the surface and interface where oxidation into arsenate takes place, though the precise oxidation mechanism is yet to be understood.

#### 7.5 Final Remarks

In this section advanced characterization methods were used to understand the chemical environments and degradation mechanisms present in iconic artwork from the early 19th century and the early 18th century. XANES and NEXAFS, which are highspatial resolution variable X-ray energy synchrotron spectroscopies, have identified the micro-structure in carefully extracted paint samples. The distributions and chemical speciation of paint particles and likely degradation by-products were precisely characterized. These approaches can be applied to any variety of chemical systems and undoubtedly more museums will recognize the importance in this sort of research. Unfortunately, degradation of these historic paintings is likely from exposure to environmental conditions; which means appreciation of the work by the public is not always conducive to the best preservation practices.

#### Chapter 8

#### CONCLUSIONS AND FUTURE WORK

#### 8.1 Conclusions

The application of synchrotron radiation to scientific research of condensed matter has been exploited a great deal in this work. With extremely high spatial resolutions and selection from a wide-spectrum of wavelengths, synchrotron capabilities are unmatched by any other laboratory setting. In this dissertation a synchrotron spectroscopy known as HAXPES was used to understand the influence of chemical environments on electrical properties in electronic materials. Additionally, another synchrotron spectroscopy, XANES, was used to elucidate the chemical speciation in pigments from iconic and historical artworks.

Improved processing of electronic materials has aided in the transition to smaller and more complex geometries. Thin film deposition methods and chemistries for electronic materials were introduced in Chapter 2; zirconium organo-metallics and oxygen containing precursors were highlighted due to potential use of  $ZrO_2$  as a replacement gate dielectric. It was discovered that the thermal stability of precursors for ALD growth of  $ZrO_2$  films can be increased by selectively substituting ligands; in the dissertation cyclopentadienyl ligands and alkoxide ligands were used.

Characterization methods of deposited electronic materials were discussed in Chapters 3-6. The standard XPS approach for studying chemical and electrical environments in thin films was expanded to include HAXPES and VKE-XPS. HAXPES and VKE-XPS improve upon the limited XPS probing depth by about an order of magnitude. Moreover, deeper atomic core-levels are available and X-ray energies are adjustable with synchrotron based techniques. One of the challenges, however, is a precise determination of the in-situ X-ray beam energy. A new calibration procedure was introduced and instituted for each of the HAXPES and VKE-XPS experiments. Benefits of extended probing depths were first demonstrated by HAXPES. By studying band bending caused by buried electrical environments in a MOS stack of Ti/Al<sub>2</sub>O<sub>3</sub>/Si the investigation concluded that peak energy shifts, or band bending, was caused by the existence of an electric dipole between the oxide and silicon substrate. VKE-XPS, a collection of HAXPES experiments, attenuates the electron intensities from buried layers by adjusting the X-ray energy. A statistical algorithm, Bayes-Sim, was developed to collect results from VKE-XPS and reconstruct compositional depth profile fits based on the data. Each fit's goodness or confidence value is evaluated against other potential CDPs. J-FAB, a new computational software package, provides a platform to prepare the synchrotron data and interface with users to run the Bayes-Sim algorithm.

Finally, this dissertation was punctuated by efforts to combine the extensive capabilities of synchrotron radiation for material studies and the ongoing investigations of degrading artworks. Collaborators from the Winterthur Museum (Newark, Delaware), the Barnes Foundation (Philadelphia, Pennsylvania), and The University of Amsterdam (The Netherlands) have been leading efforts to protect iconic works of art, like those of Henri Matisse and Adriaen Coorte - a Still Life artist from early 18th century. This work's contributions have led to a better understanding of these paint systems on a micro-scale. Using XANES and XRF chemical constituents were identified and degradation processes were proposed. Matisse's cadmium yellows from *Le Bonheur de vivre* (CdS) have likely decomposed into CdSO<sub>4</sub> as a result of photo-oxidation. Coorte's arsenic sulfide pigments from *Still Life with Five Apricots* have likely undergone oxidation as well, leading to pigment mobilization and friability.

In summary, this dissertation utilized advanced spectroscopic measurements at synchrotron beamlines to investigate and model the distribution and effects of chemical compositions within condensed matter systems.

#### 8.2 Final Remarks and Future Work

#### 8.2.1 CDP Statistical Modeling

Though effective for comparative analysis the Bayesian probabilistic calculations are somewhat limited by the reference knowledge already available. In part, this is due to the information available from XPS methods; they will always be surface sensitive compared to the deeper regions. The transformation from a CDP to an XPS intensity data sets (e.g. HAXPES or VKE-XPS) is a many-to-one mapping and can therefore provide multiple equivalently "good" fits. It is ultimately up to the knowledge of the user to eliminate non-physical results and direct simulations towards reasonable output without influencing the sampling too strongly. It is difficult to quantify what the exact limitations of the Bayes-Sim algorithm is, but for this work it has been shown that a reasonable amount of knowledge about a material system can provide informative models.

#### 8.2.2 Paint Degradation

Often it is hard to provide conclusive evidence for the mechanisms behind the discussed paint degradations; information about the chemical syntheses used by the painter, storage environments, and protective treatments used in the past are always going to be somewhat incomplete. In an attempt to "re-create" the starting conditions efforts have begun to synthesize paint reconstructions for Matisse's cadmium yellows and then artificially age them using a heating process. Additionally, other works from the same time period which possess similar yellows have also shown decomposition. Recently, samples from yellows in Edvard Munch's *The Scream* (1910) have been obtained and are seen as a potential match to paints used in *Le Bonheur de vivre*. Correlating similar mechanisms and chemical speciations between the two could be a significant finding for these and other artworks.

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## Appendix

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Figure A.1: Permission letter for Fig. 1.4

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#### Figure A.2: Permission letter for Fig. 1.8



Figure A.3: Permission letter for excerpts from Section 4.2

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### Figure A.4: Permission letter for Fig. 4.1, Fig. 4.2, Table 4.1

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